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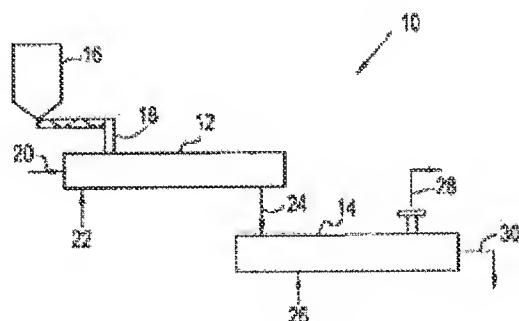
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(54) METHOD FOR CONTINUOUSLY MANUFACTURING HEAT- VULCANIZABLE SILICONE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for obtaining a homogenous filler compounded heat-vulcanizable silicone composition having required reinforcing characteristics and a volatile component level by compounding high levels of a filler, a processing fluid and a silicone polymer.

SOLUTION: High levels of treated fumed silica, processing fluid and high molecular weight silicone polymer are continuously compounded into a homogenous silica filled heat-vulcanizable silicone composition by forming a premix in a continuous annular layer mixer and continuously discharging the premix into a compounding apparatus to form the filled heat-vulcanizable silicone composition.



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CLAIMS

[Claim(s)]

[Claim 1] It is the compounding method of a filler combination thermosetting silicone composition, A method including that method concerned supplies a filler and silicone polymer to a high-speed mixing stage continuously, forms a free fluid granular concentrate, and discharges the above-mentioned free mobility granular concentrate from a mixing stage continuously to compounding equipment.

[Claim 2] A method according to claim 1 including carrying out compounding of said concentrate continuously within said compounding equipment, and forming a filler combination thermosetting silicone composition.

[Claim 3] A way according to claim 1 said mixing stage consists of shearing and an agitator style.

[Claim 4] A way according to claim 1 said mixing stage contains a continuation annular layer mixer.

[Claim 5] A way according to claim 1 said compounding equipment is a spiral drive extrusion machine style.

[Claim 6] Two continuation annular mixers which said mixing stage connected in series are included, A method according to claim 1 of mixing a filler with silicone polymer in a continuation annular layer mixer by holding time for about 5 seconds ~ about 10 minutes, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 7] Two or more continuation annular mixers which said mixing stage connected in series are included, A method according to claim 1 of mixing a filler with silicone polymer in a continuation annular layer mixer by holding time for about 10 seconds ~ about 5 minutes, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 8] Two continuation annular mixers which said mixing stage connected in series are included, A method according to claim 1 of mixing a filler with silicone polymer in a continuation annular layer mixer by holding time for about 20 seconds ~ about 3 minutes, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 9] A way according to claim 1 said mixing stage is a continuation annular layer mixer, and said compounding equipment is a spiral drive extrusion machine style.

[Claim 10] A method according to claim 9 by which said continuation annular layer mixer is adjoined and connected to said compounding equipment.

[Claim 11] A method according to claim 9 to which said continuation annular layer mixer is connected in contact with said compounding equipment.

[Claim 12] A method according to claim 9 of mixing a filler with silicone polymer with about 3 ~ element tip speed of about 100 m/s in said continuation annular layer mixer, forming a premix, and including discharging a premix to compounding equipment.

[Claim 13] A method according to claim 9 of mixing a filler with silicone polymer with about 10 ~ element tip speed of about 80 m/s in said continuation annular layer mixer, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 14] A method according to claim 9 of mixing a filler with silicone polymer with about 15 ~

element tip speed of about 60 m/s in said continuation annular layer mixer, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 15]A method according to claim 9 of mixing a filler with silicone polymer in said continuation annular layer mixer by holding time for about 3 seconds – about 5 minutes, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 16]A method according to claim 9 of mixing a filler with silicone polymer in said continuation annular layer mixer by holding time for about 5 seconds – about 1 minute, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 17]A method according to claim 9 of mixing a filler with silicone polymer by about 20 – holding time for about 45 seconds in said continuation annular layer mixer, forming a premix, and including discharging a premix to said compounding equipment.

[Claim 18]A way according to claim 9 said continuation annular layer mixer has at least the first section containing a mixing element, the second section containing a cutting element, and the third section containing a mixing element one by one.

[Claim 19]A method according to claim 9 of having the second section where said continuation annular layer mixer contains at least a cutting element or a neutral cutting element of the first section and an advance pitch containing a mixing element of an advance pitch, and the third section containing a mixing element of a reverse pitch one by one.

[Claim 20]A way according to claim 19 said continuation annular layer mixer contains about 5 – the first section element of 80% of abbreviation, about 10 – the second section element of 85% of abbreviation, and about 0 – the third section element of 75% of abbreviation.

[Claim 21]A way according to claim 19 said continuation annular layer mixer contains about 10 – the first section element of 65% of abbreviation, about 10 – the second section element of 65% of abbreviation, and about 10 – the third section element of 75% of abbreviation.

[Claim 22]A way according to claim 19 said continuation annular layer mixer contains about 15 – the first section element of 55% of abbreviation, about 10 – the second section element of 45% of abbreviation, and about 20 – the third section element of 65% of abbreviation.

[Claim 23]A way according to claim 19 said continuation annular layer mixer also includes further the last section containing a cutting element of an advance pitch, or a mixing element of an advance pitch.

[Claim 24]It is the compounding method of a filler combination thermosetting silicone composition, A method including that method concerned mixes a filler with silicone polymer with about 3 – element tip speed of about 100 m/s in a continuation annular layer mixer, forms a premix, and discharges a premix to processing equipment of the following.

[Claim 25]A way according to claim 24 said tip speed is about 10 – about 80 m/s.

[Claim 26]A way according to claim 24 said tip speed is about 15 – about 80 m/s.

[Claim 27]How to be the method of forming a premix for filler combination thermosetting silicone composition manufacture, and include that method concerned mixes a filler with silicone polymer in a continuation annular layer mixer, and discharges a filler combination silicone polymer premix from a mixer.

[Claim 28]A method according to claim 27 of discharging said premix to a storage zone.

[Claim 29]A method according to claim 27 of discharging said premix and conveying to a zone for processing it further.

[Claim 30]A method according to claim 27 of discharging said premix and conveying to a zone for processing it further.

[Claim 31]A continuation annular layer mixer which includes at least the first section containing a mixing element, the second section containing a cutting element, and the third section containing a mixing element one by one.

[Claim 32]The continuation annular layer mixer according to claim 31 which includes the second section that contains at least a cutting element or a neutral cutting element of the first section and

an advance pitch containing a mixing element of an advance pitch, and the third section containing a mixing element of a reverse pitch one by one.

[Claim 33]The continuation annular layer mixer according to claim 31 containing about 5 – the first section element of 80% of abbreviation, about 10 – the second section element of 85% of abbreviation, and about 0 – the third section element of 75% of abbreviation.

[Claim 34]The continuation annular layer mixer according to claim 31 containing about 10 – the first section element of 65% of abbreviation, about 10 – the second section element of 65% of abbreviation, and about 10 – the third section element of 75% of abbreviation.

[Claim 35]The continuation annular layer mixer according to claim 31 containing about 15 – the first section element of 55% of abbreviation, about 10 – the second section element of 45% of abbreviation, and about 20 – the third section element of 65% of abbreviation.

[Claim 36]The continuation annular layer mixer according to claim 31 which also includes further the last section containing a cutting element of an advance pitch, or a mixing element of an advance pitch.

[Claim 37]Compounding equipment including a continuation annular layer mixer of the first step, and the one or more latter parts containing an extrusion machine connected with the first step so that a processing material could be continuously discharged from the first step to a second stage.

[Claim 38]The compounding equipment according to claim 37 with which a continuation annular mixer of the first step has at least the first section containing a mixing element, the second section containing a cutting element, and the third section containing a mixing element one by one.

[Claim 39]. Have the second section where a continuation annular mixer of the first step contains at least a cutting element or a neutral cutting element of the first section and an advance pitch containing a mixing element of an advance pitch, and the third section containing a mixing element of a reverse pitch one by one. The compounding equipment according to claim 37.

[Claim 40]a continuation annular mixer of the first step — about 5— about 80% of the first section element, and about 10— about 85% of the second section element, and about 0— the compounding equipment according to claim 37 containing about 75% of the third section element.

[Claim 41]a continuation annular mixer of the first step — about 10— about 65% of the first section element, and about 10— about 65% of the second section element, and about 10— the compounding equipment according to claim 37 containing about 75% of the third section element.

[Claim 42]a continuation annular mixer of the first step — about 15— about 55% of the first section element, and about 10— about 45% of the second section element, and about 20— the compounding equipment according to claim 37 containing about 65% of the third section element.

[Claim 43]The compounding equipment according to claim 37 with which a continuation annular mixer of the first step also includes further the last section containing a cutting element of an advance pitch, or a mixing element of an advance pitch.

[Claim 44]The compounding equipment according to claim 38 which cuts off the corners inside and makes a cutting edge while said mixing element's containing a stem, and having extended to a distance sector head of the termination, and said cutting element's containing a stem and opening outside with the distance head.

[Claim 45]The compounding equipment according to claim 37 with which said second stage contains the geared type said direction rotation twin screw extruder.

[Claim 46]The compounding equipment according to claim 37 with which said second stage contains the non-engagement type said direction rotation twin screw extruder.

[Claim 47]The compounding equipment according to claim 37 which is an adjoining stage with said separate stage.

[Claim 48]The compounding equipment according to claim 37 which is a stage which said stage touches continuously.

[Claim 49]The compounding equipment according to claim 37 containing two or more mixers which the first step has arranged in series.

[Claim 50]The compounding equipment according to claim 37 which the first step contains two or more mixers, and is arranged so that two or more mixers may operate to a tandem.

[Claim 51]The compounding equipment according to claim 37 with which said one or more latter parts consist of the geared type said direction rotation twin screw extruders, different direction rotation twin screw extruders, or single screw extruders.

[Claim 52]The compounding equipment according to claim 37 with which said one or more latter parts consist of geared type said direction rotation twin screw extruders or both-way formula single screw extruders.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the method of manufacturing a thermosetting silicone composition continuously.

[0002]

[Description of the Prior Art] The thermosetting silicone composition contains the various additive agents which give desired final characteristics to hyperviscous silicone polymer, the inorganic filler for reinforcement, and processing aid and other constituents. If a vulcanized agent is added and a constituent is heat-hardened, a gasket, a medical tubing, and silicone rubber mold goods like a computer keypad can be manufactured.

[0003]A thermosetting silicone composition is manufactured by mulling hyperviscous polydyorganosiloxane, an inorganic filler, and an additive agent usually by a batch type kneader like a high intensity Banbury mixer or a low-strength double arm type dough mixer. In this method, it mixes with a batch method until the characteristic of a request of polydyorganosiloxane, an inorganic filler, a processing agent, and an additive agent is obtained. In US,5198171,B besides Kasahara, the pre concentrate of polydyorganosiloxane, an inorganic filler, and a processing agent is formed by a high-speed mechanical shearing mixer. Compounding of the obtained premix is further carried out with the direction rotation twin screw extruder. A premix is formed in the first step that provides the fluid granulated mixture which mixes diorganopolysiloxane, inorganic filler, and processing agent which have the viscosity more than 1×10^5 cP at 25 ** with a high-speed machine shearing machine, and in which each ingredient exists in the state of uniform fine dispersion substantially.

Subsequently to the direction rotation 2 axis extruding kneading machine, a fluid granulated mixture is supplied with a fixed speed of supply.

[0004]Long mixing time and a lot of energy are needed for a batch type process. In whole batch of commercial scale, it becomes uneven, the particle size distribution of a filler becomes uneven, and shearing and elongation stress may produce variation in the characteristic. The batch processed at a different stage may differ in physical properties variously. A batch process consumes a labor, energy, and capital in large quantities, and, moreover, only produces the substance of the consistency in front of a limit.

[0005]At US,5409978,B besides Hamada, the pre concentrate of polydyorganosiloxane, an inorganic filler, and a processing agent is formed at the temperature of about 200–300 ** with a said direction rotation 2 axis continuous extrusion machine. It ranks second, and compounding of the pre concentrate is carried out with a different direction rotation twin screw extruder, and it is heat-treated at 150–300 **. However, the process of requiring two extrusion machines is expensive, and needs a work area big moreover.

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[Problem to be solved by the invention] However, the throughput is restricted by these methods.

While giving the throughput which improved, the method of fitting as a low cost process which is continuously consistent and can produce the silicone elastomer covering the whole region of hypoviscosity thru/or hyperviscosity from a filler, an additive agent, and polymer using a single extrusion machine efficiently is needed.

[0007]

[Means for solving problem] This invention provides the method of obtaining the uniform filler combination thermosetting silicone composition which carries out compounding of the filler, processing fluid, and silicone polymer of a high level, and has the necessary reinforcement characteristic and volatile-matter-content level. In this method, a filler and silicone polymer are continuously supplied to a high-speed mixing stage, and a free fluid granular concentrate is formed. From a mixing stage, this concentrate is continuously discharged to compounding equipment, and processing treatment is further carried out to it.

[0008] In another mode, this invention relates to the method of forming the premix of a filler and silicone polymer. In this method, a filler is mixed with silicone polymer by a continuation annular layer mixer, and this filler combination silicone polymer premix is discharged from a mixer.

[0009] In another mode, this invention relates to the method of carrying out compounding of the filler combination thermosetting silicone composition. In this method, a filler is mixed with silicone polymer with about 3 – the element tip speed of about 100 m/s in a high-speed continuous mixer. Next, this premix is discharged to the processing treatment equipment of the following.

[0010] In another mode, this invention relates to the continuation annular layer mixer which has the second section that contains at least the cutting element of the first section, a neutral, or an advance pitch containing the mixing element of an advance pitch, and the third section containing the mixing element of a reverse pitch one by one.

[0011] In another mode, this invention relates to compounding equipment including a continuation annular layer mixer of the first step, and the one or more latter parts containing an extrusion machine connected with the first step so that a processing material could be continuously discharged from the first step to a second stage.

[0012]

[Mode for carrying out the invention] A Banbury mixer or a dough mixer is known as an object for batch type compounding of a filler and silicone polymer. This compounding work has two separate stages, a filler is soaked in polymer, on a second stage story, an aggregate is crushed finely and a filler is uniformly distributed in polymer in the first step. It is important that a filler fully distributes to polymer. Since a big aggregate which is not distributed may act as a defect which causes destruction, it will be inferior to a mechanical property.

[0013] In a batch type or a continuous system process, a processing agent can be distributed together with silicone polymer before the time of addition of a filler, or addition. In these processes, big interface power occurs between silicone polymer and an unreacted silanol group of isolation which exists in a filler. For processing, a processing agent must be diffused in a lot of amount silicone polymer of polymers, must permeate stiffened silicone polymer / filler interface, and must reach a filler. It is necessary to increase mixing intensity so that a processing agent may permeate and big interface power for approaching a silanol group may be overcome. Increase of mixing intensity causes a rise of inconvenient material temperature.

[0014] In this invention, a free fluid granular concentrate of silicone and a filler is formed continuously in a high-speed mixing stage. In order to carry out processing treatment of this concentrate further, it discharges from a mixing stage continuously to compounding equipment. The mixing stage shall consist of a continuation annular layer mixer. A continuation annular layer mixer includes a cylindrical shape mixing trough, and a mixed material contacts a cylindrical shape mixer wall, and follows a spiral course in accordance with a trough axis annularly. A typical continuation annular layer mixer is indicated by US,5018673,B besides Eric. A mixer which contains in this United States patent cylindrical shape housing arranged horizontally substantially is indicated, a material

supplying pipe for supplying material to the first end of housing continuously is formed, and a material exhaust pipe for taking out material continuously is formed in that second end. Cylindrical shape housing has surrounded mixed equipment arranged in this housing at the same axle. Mixed equipment may be driven at high speed. This equipment has projected [to / from equipment / near the housing wall] a mixed implement to an abbreviation radial direction including a mixed implement. This mixer includes a supplying zone connected with a material supplying pipe, and a humidification zone established in the transportation direction lower stream of shaft orientations of a supplying zone. A means for making a liquid advance into annular material at this mixer is formed in a humidification zone. On a housing wall, annular material is conveyed spirally and moves in inside of a mixer. A mixer includes conglomerate separating mechanism further. This means is the cutting tool formed in a radial flat surface to a shaft of mixed equipment, and contains two or more cutting tools arranged at equal intervals over the perimeter of housing.

[0015]According to one embodiment of this invention, a fine dispersion object of unhardened silicone polymer is formed in a filler of the specified quantity, using a continuation annular layer mixer as a reserve mixing stage. This material will rank second, and a phase transformation will be carried out under compression and extension / shearing flow field in an extrusion machine, it will be in a compound state, and a dry filler is in a minority group's phase. Mixing time within an extrusion machine is shortened by eburnation in the first step, and productivity is substantially improved by it.

[0016]As long as an inorganic filler which can be used by this invention is an inorganic filler used for a blend with silicone polymer, what kind of thing may be sufficient as it. There is silica which carried out the surface treatment with an organic silicon compound like fumed silica, silica for reinforcement like precipitated silica or organopolysiloxane, organoalkoxysilane, organochlorosilane, or hexa ORGANO disilazane in an example of an inorganic filler. A filler may be diatomaceous earth, pulverizing quartz, an aluminum oxide, titanium oxide, iron oxide, cerium oxide, hydroxylation cerium, magnesium oxide, a zinc oxide, calcium carbonate, zirconium silicate, carbon black, or ultramarine. Since silicone polymer is reinforced, combination of a filler of a single kind or a filler can be used.

[0017]quantity of a filler --- about 5 per silicone polymer 100 weight section - about 200 weight sections --- desirable --- about 10- it can be preferably considered as about 20 - about 60 weight sections about 100 weight sections.

[0018]A remains silanol group on the surface of a filler may govern intensity of a hydrogen bond with silica, hydroxyl of a silicone polymer chain, or an oxygen group. If a high-concentration remains silanol exists in a filler, "structure formation" or "crepe hardening" of a final product will be caused at the time of storage. This effect makes difficult processing of material after carrying out long-term storage. When concentration of silanol functional groups of a filler is too high, a silanol group can be lowered to required density by addition of a processing agent. The silanol reagin processing agent can react to an effective group, and the unit area (square NANOMETORU) per hydroxyl 8 [about] of a filler - two abbreviation can lower concentration to about 7 - three abbreviation preferably. surface treatment silica is a desirable filler in this invention --- the quantity --- per silicone polymer 100 weight section --- about 10- they are about 20 - about 60 weight sections preferably about 100 weight sections.

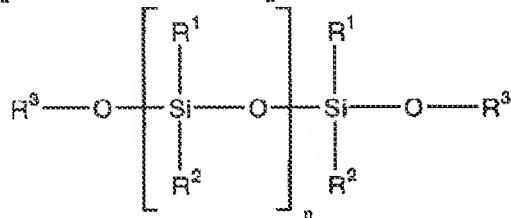
[0019]If a processing agent is mixed to a filler, a silanol group of a filler can be reduced, time required for an improvement and/or aging of silicone rubber can be shortened for the dispersibility of a filler, and prevention and/or plasticity can be adjusted for crepe hardening. A processing agent can be made into an organosilane, a hypoviscosity polysiloxane, or silicone resin, and has a silanol group and/or an alkoxy group with 1-6 carbon atoms. As an example, there are diphenyl-Silang diol, dimethylsilane diol, methyl triethoxysilane, and phenyltrimethoxysilane. A hypoviscosity polysiloxane may contain one or more kinds of organic groups chosen from a methyl group, a phenyl group, a vinyl group, and a 3,3,3-trifluoropropyl group. viscosity of a polysiloxane measured at 25 ** --- about 1- they are about five to about 100 cP(s) preferably about 300 cP. a processing agent --- 0.1 per filler 100 weight section - 100 weight section --- desirable --- 0.5- it can add in quantity of about 1.0

~ about 20 weight sections preferably about 50 weight sections. As a desirable silanol reagent processing agent, there are a silanol end polydimethyl siloxane, octamethylcyclotetrasiloxane (D4), and hexamethyldisilazane (HMDZ).

[0020]Silicone polymer used for a constituent of this invention can be expressed with a repeating unit of the following formula I.

[0021]

[Chemical formula 1]



式 I

[0022] R^1 expresses C_{1-4} alkyl or a C_{2-4} alkylene independently respectively among a formula, R^2 expresses C_{1-4} alkyl, C_{1-4} halo alkyl, or a C_{2-4} alkylene independently respectively, R^3 expresses H, C_{1-10} alkyl, a C_{2-4} alkylene, C_{4-6} cycloalkyl, OH, or C_{1-4} halo alkyl independently respectively, and n expresses an integer of 1000~20000.

[0023]As for a still more desirable constituent, R^1 expresses CH_3 or $CH=CH_2$ independently respectively, R^2 expresses CH_3 , $CH=CH_2$, or $CH_2CH_2CF_3$ independently respectively, Silicone polymer as which R^3 expresses CH_3 , $CH=CH_2$, OH, or $CH_2CH_2OF_3$ independently respectively, and n expresses about 4000 ~ about 10000 integer is included.

[0024]According to another embodiment, a constituent whose vinyl contents of silicone polymer are about 0.05 of silicone polymer ~ 0.5 weight % of abbreviation is provided.

[0025]A heat-resistant improver [like a metaled oxide, hydroxide, and fatty acid salt] whose thermosetting silicone composition is, Other additive agents like a vulcanization return inhibitor, fire retardant like a platinum compound, an antitarnish agent, a plasticizer like silicone oil, an internal release agent like metallic soap, paints, and a color may be included.

[0026]Although I will become clear [the feature of this invention] from attached Drawings and the following detailed explanation, these are for illustrating an embodiment of this invention, and do not limit this invention.

[0027]Drawing 1 shows an outline of a method of this invention.

[0028]By drawing 1, equipment of this invention contains the high-speed mixing stage 12 and the extrusion machine stage 14. A continuation annular layer mixer may be sufficient as it, and even if the high-speed mixing stage 12 is a single mixer, they may be two or more mixers arranged in series. The extrusion machine stage 14 can be made or more [of the geared type said direction rotation twin screw extruder, a different direction rotation twin screw extruder, or a single screw extruder] into one. Preferably, the extrusion machine stage 14 is the geared type said direction rotation twin screw extruder or a both-way formula single screw extruder. When an extrusion machine stage contains two or more extrusion machines, it can connect with series or a tandem.

[0029]In the method of this invention, a filler is accommodated in the loss-in-quantity feeder 16, and is supplied to the mixing stage 12 with the silicone polymer 20 and the processing agent 22 18.

[0030]In the mixing stage 12, polymer, a filler, and a processing agent are given to powerful power at high speed, and produce the free fluid powder premix 24. Material is ground finely, and while covering

a filler with polymer, in order to soak material in a processing agent, suitable tip speed and holding time are needed. What is necessary is just to mix material with about 3 – the element tip speed of about 100 m/s, in order to form a premix. desirable --- element tip speed --- about 10 – about 80 m/s --- desirable --- about 15 – it is about 60 m/s. Holding time is time taken for material to pass a mixer. Holding time can be made into about 3 seconds – about 5 minutes (min) when using a single mixer. the holding time about a single mixer --- about 5s – they are about 20 s – about 45 s preferably about 1 min. The mixing stage 12 may contain two or more mixers. when using two mixers in series, the holding time about two sets may be about 5 s – about 10 min --- carrying out --- or holding time --- about 10s – it can be preferably referred to as 20 s – about 3 min about 5 min. In the mixing stage 12, tap density 0.3 [about] – about 0.6 or about 0.35 – about 0.55, further 0.36 – about 0.48 output may be produced.

[0031]Storage distribution may be carried out, in order to be also able to use the premix 24 for a convenient thing with a continuous magnetization method (it illustrated like) or to use it for it later. The premix 24 is supplied to the extrusion machine stage 14 by drawing 1, compounding is carried out to the additive agent 26 there, volatile matter content is removed, and the thermosetting silicone polymer constituent 30 is produced.

[0032]Another embodiment of this invention is shown in drawing 2. The equipment 50 of drawing 2 contains the continuation annular layer high speed mixer 52 and the second mixer 54 arranged in series. In order to extend holding time and to obtain a premix with little variation, two or more mixers may be used. Equipment of drawing 2 contains the extrusion machine 56 and the extrusion machine 58 connected in series downstream from the mixers 52 and 54.

[0033]In a method shown in drawing 2, weighing of the filler 62 is carried out with the loss-in-quantity feeder 60, and it puts into the first mixer 52, and mixes with the polymer 62 and the processing agent 66. Output of the mixer 52 is supplied to the mixer 54 by 68, and the free fluid powder premix 70 arises there. It is supplied to the extrusion machine 56, and in order to carry out filler processing further there, an additional processing agent is added by 72. In order to manufacture low durometer material, additional polymer (not shown) may be added in this stage. Processing aid and other additive agents are added in this stage 74, the output 76 is acquired, it is supplied to the extrusion machine 58, and volatile matter content is excluded by 78. What is necessary is just to use it, since the thermosetting silicone polymer constituent 80 is obtained with the extrusion machine 58.

[0034]A continuation annular layer mixer and an attached element are shown in drawing 3 – drawing 8.

[0035]A processing element with which a mixer which can be used by this invention can be equipped is shown in drawing 4 and drawing 5. Drawing 3 is a side elevational view of the continuation annular layer mixer 102 in which arrangement of an element of drawing 4 and drawing 5 is shown.

[0036]By drawing 3, the mixer 102 contains in a center the cylindrical shape housing 104 which has the longitudinal direction shaft 106. As for the housing 104, both ends are closed by the end wall 108,110. The shaft 106 penetrated both ends of the housing 104, has projected, and is closed by the end wall 108,110. The material supply port 112 is attached to the upper part of the housing 104, and are open to a nearly contacting line direction toward housing 104 inside, A lower end of the housing 104 is equipped with the outlet 114 toward an inside of the housing 104 in a nearly contacting line direction, and it is wide opened from an inside of the housing 104.

[0037]A processing element of various designs is provided in the shaft 106 of the mixer 102. Drawing 4 extends from the rotating shaft 106, and shows the mixing element 116 which has projected radially from the shaft 106 within the continuation annular layer mixer 102 of drawing 3. The mixing element 116 has aligned at intervals of 90 degrees in shaft orientations as it is shown in ****, drawing 7, and drawing 8 at the shaft 106, i.e., a longitudinal direction axis. The mixing element 116 contains the stem 118 which extends from the base 120 to the distance sector head 122 of a termination. The illustrated mixing element 116 extends vertically to the base 120, and has the

paddle head 122 to which an angle was attached. According to a case, since the element 116 increases comparatively a conveyance (promotion) function or a back-mixing function, it is fixed to the base 120 by a predetermined head helix angle. explanation of a pitch with various elements and a function is boiled and explained with reference to drawing 6 – drawing 9 later.

[0038]It extends in drawing 5 from the base 126, and the cutting element 124 radially prolonged from the shaft 106 within the mixer 102 is shown in it. the cutting element 124 contains the stem 128 — the distance head 136 — the outside — opening (130) — it cuts off the corners inside (132) and the cutting edge 134 is made. The illustrated element 124 has extended vertically. Since the element 124 adjusts a carrying function and a back-mixing function so that it may explain with reference to drawing 6 – drawing 9, it can be fixed by a predetermined cutting edge helix angle. The element 124 has aligned at intervals of 90 degrees in shaft orientations as it is shown in **** and drawing 8 at the shaft 106, i.e., a longitudinal direction axis.

[0039]Drawing 6 is an approximate account figure of an element, and shows a pitch of an element about the mixer shaft 106. In the first supply section (the first section) 138 of the mixer 106 shown in drawing 6, the mixing element 140 which set a head to the axial transportation direction 142 is formed. The filler / processing agent / silicone polymer of a raw material are supplied to the first section 138 of the mixer 106 via the feed hopper 112 shown in drawing 3, and is accelerated and conveyed by the mixing element 140 in the axial transportation direction 142. Drawing 6 shows a pitch of the element heads 122 and 136 seen from an axis formed with the longitudinal direction axis 152 of the mixer shaft 106, and is defined by size drawing 9 of a pitch. An element with not less than 90-degree the helix angle below 180 degrees gives a carrying function, and an element with 0-degree or more the helix angle below 90 degrees gives a retaining function. The mixing element 140 has estranged the mixing element 140 at intervals of about 90 degrees in accordance with the circumference of the shaft 106 as it has extended to near the housing 104 wall so that a dead space may not be produced, and shown in drawing 7.

[0040]The mixing element 140 is set to a transportation direction at an angle of about 138 degrees from perpendicularly it defines as the compass 146 of drawing 9. In accordance with the longitudinal direction axis 150 of a mixer shaft, the vertical axis 152 of the horizontal axis 148 is vertical to the axis 150 at drawing 9. A centrifugal force arises, material is thrown off by rotation of the conveyance element 140, and it becomes an annular form by a radial outer edge of the element 140 by it. Subsequently, an annular feed material will follow mixer 102 inside spirally with a pitch of the element 140.

[0041]The second section 154 of the mixer 102 contains the cutting element 156 which has a pitch with a transportation direction angle of about 118 degrees from a perpendicular. The cutting element 156 is estranged at an angle of about 90 degrees to a circumferencial direction by the shaft 106 circumference as it is shown in drawing 9 with the conveyance element 140, and it has extended to near the wall of the housing 104 so that a dead space may not be produced. The element 156 achieves an operation which separates a conglomerate of material and promotes **** of a filler.

[0042]The third section 158 contains the conveyance element 160 of a reverse pitch in order to aim at extension of back mixing and holding time.

[0043]According to one embodiment of this invention, the continuation annular layer mixer 102 has at least the first section containing a mixing element, the second section containing a cutting element, and the third section containing a mixing element one by one. This section may be added to an above-mentioned mixing element or a cutting element, and may contain other elements. For example, the second section may contain a cutting element and a mixing element. The first section may contain an element of an advance pitch, the second section may contain a front element and a neutral element, and the third section may contain an element of a reverse pitch so that it may increase holding time. The whole element of the continuation annular layer mixer 102. What consists of about 5 – the first section element of 80% of abbreviation, about 10 – the second section element of 85% of abbreviation, and about 0 – the third section element of 75% of abbreviation may be used.

May consist of about 10 – the first section element of 65% of abbreviation, about 10 – the second section element of 65% of abbreviation, and about 10 – the third section element of 75% of abbreviation desirably, and, It may consist of about 15 – the first section element of 55% of abbreviation, about 10 – the second section element of 45% of abbreviation, and about 20 – the third section element of 65% of abbreviation preferably.

[0044]The first section 138 where drawing 6 shows one embodiment of this invention, and the continuation annular layer mixer 102 consists of the mixing element 140 of an advance pitch, It has the second section 154 that consists of the cutting element 156 of an advance pitch, and the third section 158 that consists of the mixing element 160 of a reverse pitch one by one. A termination of the mixer 102 is good also as the fourth section 162 that consists of the cutting element 164 of a reverse pitch for discharging a premix, and the following neutral element 168 as shown in drawing 6. The second section 154 may contain the mixing element 166 of an advance pitch.

[0045]In this invention, what unhardened silicone polymer distributed minutely in a filler of the specified quantity is obtained by carrying out preliminary mixing by a continuation annular layer mixer. This material will rank second, and a phase transformation will be carried out under compression and extension / shearing flow field in an extrusion machine, it will be in a compound state, and a dry filler is in a minority group's phase. Mixing time is shortened by eburnation of a filler within an annular layer mixer, and productivity is substantially improved by it.

[0046]These features and the other features will become clear from the following detailed explanation that describes the desirable embodiment of this invention in the sense of illustration, without limiting. In the following embodiments, premix quality is characterized with the particle size in tap density, BET surface area, a solution, and the end of dried powder. A premix material is inspected by the scanning electron microscope, the transmission electron microscope, and a compression test.

[0047]

[Working example]The element of composition of having indicated to Table 1 is provided in an example 1 Drees (Drais)KTT continuation annular layer mixer.

Table 1 element number / explanation angle * theory . ** 1 139 Front conveyance and mixing element . 2 136 front conveyance and mixing element 3. 139 Front conveyance and mixing element 4 135. Front conveyance and mixing element 5 119 Front conveyance / cutting element 6 117 Front conveyance / cutting element 1 122 Front conveyance and mixing element 8 62 Back mixing element 9 68 Back mixing element 10. 71 Back mixing element 11 70 Back mixing element . 12 70 back mixing element 13 69. Back mixing element 14 69 Back mixing element . 15 67 Back mixing element 16 67 Back mixing element 17 124 Front conveyance / cutting element 18 185 Angle from the perpendicular defined by the compass 146 of neutral cutting element * drawing 9 (degree) Use the Doling (Doering) pump (p= 240 psi) for the above-mentioned mixer, and silicone raw rubber is supplied to it at 40 pounds (lbs/hr)/o'clock in speed, Pretreatment fumed silica is supplied at the rate of 60 lbs/hr using a loss-in-quantity type AKURISON (Acrisson) feeder. Any feed is a room temperature. A mixer is operated by 3000 rpm and the amperages 15.5–16.5. Discharging temperature is raised to 81–89 degrees F, and shell temperature is kept at about 73 degrees F. A sample whose tap density is seven, 0.40–0.42, is prepared.

[0048]The Drees mixing stage of Example 1 is repeated using 63 copies of example 2 fumed silica, and 100 copies of polymer crude rubber. Promptly, feed output of the Drees mixing stage into a Banbury mixer, and Methoxy distal flow object processing agent 2.5 copy, After carrying out compounding to 2.5 copies of a silanol fluid processing agent / processing aid, and 0.8 copy of vinyl methoxysilane cross linking agent, it is made to harden for 10 minutes at 350 degrees F using 1.2 copies of catalysts, and postcure is carried out at 450 degrees F. Physical properties acquired with 75 durometer products are shown in Table 2.

[0049]A filler and polymer are directly put into a Banbury mixer, compounding is carried out to the

same material, and it is made to harden like Example 2 for example 3 comparison. Physical properties acquired with 75 durometer products are shown in Table 2.

A table 2 character / example 23 Shore A hardness 72-76 It is extended and is 395, 366 100% modulus 322-355 Tensile 1277-1302 **** B 148-153 Specific gravity 1.226-1.203-example 63 copies of 4 fumed silica, and 100 copies of polymer crude rubber. It uses and the Drees mixing stage of Example 1 is repeated. Output of the Drees mixing stage is promptly fed into a Banbury mixer, and compounding is carried out to methoxy distal flow object processing agent 2.5 copy, 2.5 copies of silanol fluid processing agents / processing aid, and 0.8 copy of vinyl methoxysilane cross linking agent. Compounding of the sample which consists of such materials is carried out with a Banbury mixer of various RPM. A sample which carried out compounding is stiffened for 12 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the obtained sheet-shaped sample is carried out at 200 ** for 4 hours. Physical properties over 75 durometer sample are shown in Table 3.

Table 3 character / example RPM1400200028003200 Shore A hardness 76 77 75 75 It is extended and is 324. 347 308 323 100% modulus 410 407 385 366 Tensile 1327 1398. 1210 1220 **** B 134 126 126 130 Specific gravity 1.207 1.209 1.198 The Drees mixing stage of Example 1 is repeated using 1.199-example 63 copies of 5 fumed silica, and 100 copies of polymer crude rubber. After feeding the output of the Drees mixing stage into the geared type said direction rotation twin screw extruder continuously and carrying out compounding to it, it supplies to a both-way formula single screw extruder continuously, and uniformity and stripping are performed. The ultimate product includes three copies of sources of methylvinyl as 1.35 copies of vinylidol cross linking agents, 2.0 copies of silanol fluid processing agents / processing aid, and a cross linking agent/plasticizer. Output is volatile-matter-content <1%. Output is stiffened for 17 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the product sheet is carried out at 200 ** for 4 hours. The physical properties in 75 durometer sample are shown in Table 4.

[0050] The Drees mixing stage of Example 1 is repeated using 61 copies of example 6 fumed silica, and 100 copies of polymer crude rubber. After feeding output of the Drees mixing stage into the geared type said direction rotation twin screw extruder continuously and carrying out compounding to it, it supplies to a non-engagement type different direction rotation twin screw extruder continuously, and uniformity and stripping are performed. An ultimate product includes 0.5 copy of source of methylvinyl as 1.0 copy of a silanol fluid processing agent / processing aid, and a cross linking agent/plasticizer. Output is volatile-matter-content <1%. Output is stiffened for 17 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the product sheet is carried out at 200 ** for 4 hours. Physical properties in 40 durometer sample are shown in Table 4. a table — 4 character / example 56 Shore A hardness 70.1 being extended 37.8 — 327 519 100% modulus 420 108 tension 1467 1078 **** B 123 69 specific-gravity 1.21 1.106 — as a result of these shows, If a premix is prepared continuously in a high-speed mixing stage, a free fluid granular concentrate is formed and it supplies to compounding equipment continuously, a thermosetting silicone composition can be prepared.

[0051]Although a desirable embodiment of this invention has been described, change and correction are possible for this invention, and it is not limited to details of an embodiment. This invention includes change and change belonging to Claims.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the method of manufacturing a thermosetting silicone composition continuously.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The thermosetting silicone composition contains the various additive agents which give desired final characteristics to hyperviscous silicone polymer, the inorganic filler for reinforcement, and processing aid and other constituents. If a vulcanized agent is added and a constituent is heat-hardened, a gasket, a medical tubing, and silicone rubber mold goods like a computer keypad can be manufactured.

[0003] A thermosetting silicone composition is manufactured by mulling hyperviscous polydyorganosiloxane, an inorganic filler, and an additive agent usually by a batch type kneader like a high intensity Banbury mixer or a low-strength double arm type dough mixer. In this method, it mixes with a batch method until the characteristic of a request of polydyorganosiloxane, an inorganic filler, a processing agent, and an additive agent is obtained. In US,5198171,B besides Kasahara, the pre concentrate of polydyorganosiloxane, an inorganic filler, and a processing agent is formed by a high-speed mechanical shearing mixer. Compounding of the obtained premix is further carried out with the direction rotation twin screw extruder. A premix is formed in the first step that provides the fluid granulated mixture which mixes diorganopolysiloxane, inorganic filler, and processing agent which have the viscosity more than 1×10^5 cP at 25 ** with a high-speed machine shearing machine, and in which each ingredient exists in the state of uniform fine dispersion substantially.

Subsequently to the direction rotation 2 axis extruding kneading machine, a fluid granulated mixture is supplied with a fixed speed of supply.

[0004] Long mixing time and a lot of energy are needed for a batch type process. In whole batch of a commercial scale, it becomes uneven, the particle size distribution of a filler becomes uneven, and shearing and elongation stress may produce variation in the characteristic. The batch processed at a different stage may differ in physical properties variously. A batch process consumes a labor, energy, and capital in large quantities, and, moreover, only produces the substance of the consistency in front of a limit.

[0005] At US,5409978,B besides Hamada, the pre concentrate of polydyorganosiloxane, an inorganic filler, and a processing agent is formed at the temperature of about 200-300 ** with a said direction rotation 2 axis continuous extrusion machine. It ranks second, and compounding of the pre concentrate is carried out with a different direction rotation twin screw extruder, and it is heat-treated at 150-300 **. However, the process of requiring two extrusion machines is expensive, and needs a work area big moreover.

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TECHNICAL PROBLEM

[Problem to be solved by the invention] However, a throughput is restricted by these methods. While giving a throughput which improved, a method of fitting as a low cost process which is continuously consistent and can produce a silicone elastomer covering the whole region of hypoviscosity thru/or hyperviscosity from a filler, an additive agent, and polymer using a single extrusion machine efficiently is needed.

[Translation done.]

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MEANS

[Means for solving problem] This invention provides the method of obtaining the uniform filler combination thermosetting silicone composition which carries out compounding of the filler, processing fluid, and silicone polymer of a high level, and has the necessary reinforcement characteristic and volatile-matter-content level. In this method, a filler and silicone polymer are continuously supplied to a high-speed mixing stage, and a free fluid granular concentrate is formed. From a mixing stage, this concentrate is continuously discharged to compounding equipment, and processing treatment is further carried out to it.

[0008]In another mode, this invention relates to the method of forming the premix of a filler and silicone polymer. In this method, a filler is mixed with silicone polymer by a continuation annular layer mixer, and this filler combination silicone polymer premix is discharged from a mixer.

[0009] In another mode, this invention relates to the method of carrying out compounding of the filler combination thermosetting silicone composition. In this method, a filler is mixed with silicone polymer with about 3 – the element tip speed of about 100 m/s in a high-speed continuous mixer. Next, this premix is discharged to the processing treatment equipment of the following.

[0010]In another mode, this invention relates to the continuation annular layer mixer which has the second section that contains at least the cutting element of the first section, a neutral, or an advance pitch containing the mixing element of an advance pitch, and the third section containing the mixing element of a reverse pitch one by one.

[0011]In another mode, this invention relates to compounding equipment including a continuation annular layer mixer of the first step, and the one or more latter parts containing an extrusion machine connected with the first step so that a processing material could be continuously discharged from the first step to a second stage.

[0012]

[Mode for carrying out the invention] A Banbury mixer or a dough mixer is known as an object for batch type compounding of a filler and silicone polymer. This compounding work has two separate stages, a filler is soaked in polymer, on a second stage story, an aggregate is crushed finely and a filler is uniformly distributed in polymer in the first step. It is important that a filler fully distributes to polymer. Since a big aggregate which is not distributed may act as a defect which causes destruction, it will be inferior to a mechanical property.

[0013]In a batch type or a continuous system process, a processing agent can be distributed together with silicone polymer before the time of addition of a filler, or addition. In these processes, big interface power occurs between silicone polymer and an unreacted silanol group of isolation which exists in a filler. For processing, a processing agent must be diffused in a lot of amount silicone polymer of polymers, must permeate stiffened silicone polymer / filler interface, and must reach a filler. It is necessary to increase mixing intensity so that a processing agent may permeate and big interface power for approaching a silanol group may be overcome. Increase of mixing intensity causes a rise of inconvenient material temperature.

[0014]In this invention, a free fluid granular concentrate of silicone and a filler is formed continuously in a high-speed mixing stage. In order to carry out processing treatment of this concentrate further, it discharges from a mixing stage continuously to compounding equipment. The mixing stage shall consist of a continuation annular layer mixer. A continuation annular layer mixer includes a cylindrical shape mixing trough, and a mixed material contacts a cylindrical shape mixer wall, and follows a spiral course in accordance with a trough axis annularly. A typical continuation annular layer mixer is indicated by US,5018673,B besides Eric. A mixer which contains in this United States patent cylindrical shape housing arranged horizontally substantially is indicated, a material supplying pipe for supplying material to the first end of housing continuously is formed, and a material exhaust pipe for taking out material continuously is formed in that second end. Cylindrical shape housing has surrounded mixed equipment arranged in this housing at the same axle. Mixed equipment may be driven at high speed. This equipment has projected [to / from equipment / near the housing wall] a mixed implement to an abbreviation radial direction including a mixed implement. This mixer includes a supplying zone connected with a material supplying pipe, and a humidification zone established in the transportation direction lower stream of shaft orientations of a supplying zone. A means for making a liquid advance into annular material at this mixer is formed in a humidification zone. On a housing wall, annular material is conveyed spirally and moves in inside of a mixer. A mixer includes conglomerate separating mechanism further. This means is the cutting tool formed in a radial flat surface to a shaft of mixed equipment, and contains two or more cutting tools arranged at equal intervals over the perimeter of housing.

[0015]According to one embodiment of this invention, the fine dispersion object of unhardened silicone polymer is formed in the filler of the specified quantity, using a continuation annular layer mixer as a reserve mixing stage. This material will rank second, and a phase transformation will be carried out under compression and extension / shearing flow field in an extrusion machine, it will be in a compound state, and the dry filler is in a minority group's phase. The mixing time within an extrusion machine is shortened by eburnation in the first step, and productivity is substantially improved by it.

[0016]As long as the inorganic filler which can be used by this invention is an inorganic filler used for the blend with silicone polymer, what kind of thing may be sufficient as it. There is silica which carried out the surface treatment with an organic silicon compound like fumed silica, silica for reinforcement like precipitated silica or organopolysiloxane, organoalkoxysilane, organochlorosilane, or hexa ORGANO disilazane in the example of an inorganic filler. A filler may be diatomaceous earth, pulverizing quartz, an aluminum oxide, titanium oxide, iron oxide, cerium oxide, hydroxylation cerium, magnesium oxide, a zinc oxide, calcium carbonate, zirconium silicate, carbon black, or ultramarine. Since silicone polymer is reinforced, the combination of the filler of a single kind or a filler can be used.

[0017]the quantity of a filler --- about 5 per silicone polymer 100 weight section -- about 200 weight sections --- desirable --- about 10- it can be preferably considered as about 20 -- about 60 weight sections about 100 weight sections.

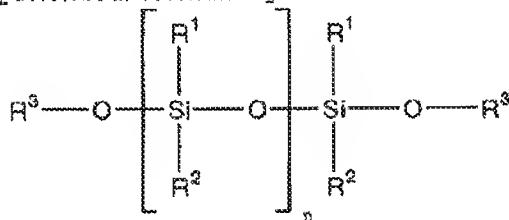
[0018] The remains silanol group on the surface of a filler may govern the intensity of a hydrogen bond with silica, the hydroxyl of a silicone polymer chain, or an oxygen group. If a high-concentration remains silanol exists in a filler, "structure formation" or "crepe hardening" of a final product will be caused at the time of storage. This effect makes difficult processing of the material after carrying out long-term storage. When the concentration of the silanol functional groups of a filler is too high, a silanol group can be lowered to required density by addition of a processing agent. The silanol reagin processing agent can react to an effective group, and the unit area (square NANOMETORU) per hydroxyl 8 [about] of a filler – two abbreviation can lower concentration to about 7 – three abbreviation preferably. surface treatment silica is a desirable filler in this invention — the quantity — per silicone polymer 100 weight section — about 10– they are about 20 – about 60 weight sections preferably about 100 weight sections.

[0019]If a processing agent is mixed to a filler, the silanol group of a filler can be reduced, time required for an improvement and/or aging of silicone rubber can be shortened for the dispersibility of a filler, and prevention and/or plasticity can be adjusted for crepe hardening. A processing agent can be made into an organosilane, a hypoviscosity polysiloxane, or silicone resin, and has a silanol group and/or an alkoxy group with 1-6 carbon atoms. As an example, there are diphenyl-Silang diol, dimethylsilane diol, methyl triethoxysilane, and phenyltrimethoxysilane. The hypoviscosity polysiloxane may contain one or more kinds of organic groups chosen from a methyl group, a phenyl group, a vinyl group, and a 3,3,3-trifluoropropyl group. the viscosity of the polysiloxane measured at 25 ** --- about 1- they are about five to about 100 cP(s) preferably about 300 cP. a processing agent --- 0.1 per filler 100 weight section - 100 weight section --- desirable --- 0.5- it can add in the quantity of about 1.0 - about 20 weight sections preferably about 50 weight sections. As a desirable silanol reagin processing agent, there are a silanol end polydimethyl siloxane, octamethylcyclotetrasiloxane (D4), and hexamethyldisilazane (HMDZ).

[0020]Silicone polymer used for a constituent of this invention can be expressed with a repeating unit of the following formula I.

[0021]

[Chemical formula 1]



卷一

[0022] R¹ expresses C₁₋₄ alkyl or a C₂₋₄ alkylene independently respectively among a formula, R² expresses C₁₋₄ alkyl, C₁₋₄ halo alkyl, or a C₂₋₄ alkylene independently respectively, R³ expresses H, C₁₋₁₀ alkyl, a C₂₋₄ alkylene, C₄₋₆ cycloalkyl, OH, or C₁₋₄ halo alkyl independently respectively, and n expresses an integer of 1000-20000.

[0023] As for a still more desirable constituent, R¹ expresses CH₃ or CH=CH₂ independently respectively, R² expresses CH₃, CH=CH₂, or CH₂CH₂CF₃ independently respectively, Silicone polymer as which R³ expresses CH₃, CH=CH₂, OH, or CH₂CH₂CF₃ independently respectively, and n expresses about 4000 – about 10000 integer is included.

[0024]According to another embodiment, the constituent whose vinyl contents of silicone polymer are about 0.05 of silicone polymer – 0.5 weight % of abbreviation is provided.

[0025]A heat-resistant improver [like a metal oxide, hydroxide, and fatty acid salt] whose thermosetting silicone composition is, Other additive agents like a vulcanization return inhibitor, fire retardant like a platinum compound, an antitarnish agent, a plasticizer like silicone oil, an internal release agent like metallic soap, paints, and a color may be included.

[0026]Although I will become clear [the feature of this invention] from attached Drawings and the following detailed explanation, these are for illustrating the embodiment of this invention, and do not limit this invention.

[0027] Drawing 1 shows the outline of the method of this invention.

[0028]By drawing 1, the equipment of this invention contains the high-speed mixing stage 12 and the extrusion machine stage 14. A continuation annular layer mixer may be sufficient as it, and even

if the high-speed mixing stage 12 is a single mixer, they may be two or more mixers arranged in series. The extrusion machine stage 14 can be made or more [of the geared type said direction rotation twin screw extruder, a different direction rotation twin screw extruder, or a single screw extruder] into one. Preferably, the extrusion machine stage 14 is the geared type said direction rotation twin screw extruder or a both-way formula single screw extruder. When the extrusion machine stage contains two or more extrusion machines, it can connect with series or a tandem. [0029]In a method of this invention, a filler is accommodated in the loss-in-quantity feeder 16, and is supplied to the mixing stage 12 with the silicone polymer 20 and the processing agent 22 18. [0030]In the mixing stage 12, polymer, a filler, and a processing agent are given to powerful power at high speed, and produce the free fluid powder premix 24. Material is ground finely, and while covering a filler with polymer, in order to soak material in a processing agent, suitable tip speed and holding time are needed. What is necessary is just to mix material with about 3 – element tip speed of about 100 m/s, in order to form a premix, desirable --- element tip speed --- about 10 – about 80 m/s --- desirable --- about 15 – it is about 60 m/s. Holding time is time taken for material to pass a mixer. Holding time can be made into about 3 seconds – about 5 minutes (min) when using a single mixer, holding time about a single mixer --- about 5s – they are about 20 s – about 45 s preferably about 1 min. The mixing stage 12 may contain two or more mixers. when using two mixers in series, holding time about two sets may be about 5 s – about 10 min --- carrying out --- or holding time --- about 10s – it can be preferably referred to as 20 s – about 3 min about 5 min. In the mixing stage 12, tap density 0.3 [about] – about 0.6 or about 0.35 – about 0.55, further 0.36 – about 0.48 output may be produced.

[0031]Storage distribution may be carried out, in order to be also able to use the premix 24 for a convenient thing with a continuous magnetization method (it illustrated like) or to use it for it later. The premix 24 is supplied to the extrusion machine stage 14 by drawing 1, compounding is carried out to the additive agent 26 there, volatile matter content is removed, and the thermosetting silicone polymer constituent 30 is produced.

[0032]Another embodiment of this invention is shown in drawing 2. The equipment 50 of drawing 2 contains the continuation annular layer high speed mixer 52 and the second mixer 54 arranged in series. In order to extend holding time and to obtain a premix with little variation, two or more mixers may be used. The equipment of drawing 2 contains the extrusion machine 56 and the extrusion machine 58 connected in series downstream from the mixers 52 and 54.

[0033] In the method shown in drawing 2, weighing of the filler 62 is carried out with the loss-in-quantity feeder 60, and it puts into the first mixer 52, and mixes with the polymer 62 and the processing agent 66. The output of the mixer 52 is supplied to the mixer 54 by 68, and the free fluid powder premix 70 arises there. It is supplied to the extrusion machine 56, and in order to carry out filler processing further there, an additional processing agent is added by 72. In order to manufacture low durometer material, additional polymer (not shown) may be added in this stage. Processing aid and other additive agents are added in this stage 74, the output 76 is acquired, it is supplied to the extrusion machine 58, and volatile matter content is excluded by 78. What is necessary is just to use it, since the thermosetting silicone polymer constituent 80 is obtained with the extrusion machine 58.

[0034]A continuation annular layer mixer and an attached element are shown in drawing 3 – drawing 8.

[0035]The processing element with which the mixer which can be used by this invention can be equipped is shown in drawing 4 and drawing 5. Drawing 3 is a side elevational view of the continuation annular layer mixer 102 in which arrangement of the element of drawing 4 and drawing 5 is shown.

[0036]By drawing 3, the mixer 102 contains in the center the cylindrical shape housing 104 which has the longitudinal direction shaft 106. As for the housing 104, both ends are closed by the end wall 108,110. The shaft 106 penetrated the both ends of the housing 104, has projected, and is closed by

the end wall 108,110. The material supply port 112 is attached to the upper part of the housing 104, and are open to the nearly contacting line direction toward housing 104 inside, The lower end of the housing 104 is equipped with the outlet 114 toward the inside of the housing 104 in the nearly contacting line direction, and it is wide opened from the inside of the housing 104.

[0037] The processing element of various designs is provided in the shaft 106 of the mixer 102.

Drawing 4 extends from the rotating shaft 106, and shows the mixing element 116 which has projected radially from the shaft 106 within the continuation annular layer mixer 102 of drawing 3. The mixing element 116 has aligned at intervals of 90 degrees in shaft orientations as it is shown in ****, drawing 7, and drawing 8 at the shaft 106, i.e., a longitudinal direction axis. The mixing element 116 contains the stem 118 which extends from the base 120 to the distance sector head 122 of a termination. The illustrated mixing element 116 extends vertically to the base 120, and has the paddle head 122 to which the angle was attached. According to a case, since the element 116 increases comparatively a conveyance (promotion) function or a back-mixing function, it is fixed to the base 120 by a predetermined head helix angle. explanation of a pitch with various elements and a function is boiled and explained with reference to drawing 6 – drawing 9 later.

[0038] It extends in drawing 5 from the base 126, and the cutting element 124 radially prolonged from the shaft 106 within the mixer 102 is shown in it. the cutting element 124 contains the stem 128 -- the distance head 136 -- the outside -- opening (130) — it cuts off the corners inside (132) and the cutting edge 134 is made. The illustrated element 124 has extended vertically. Since the element 124 adjusts a carrying function and a back-mixing function so that it may explain with reference to drawing 6 – drawing 9, it can be fixed by a predetermined cutting edge helix angle. The element 124 has aligned at intervals of 90 degrees in shaft orientations as it is shown in **** and drawing 8 at the shaft 106, i.e., a longitudinal direction axis.

[0039] Drawing 6 is an approximate account figure of an element, and shows the pitch of the element about the mixer shaft 106. In the first supply section (the first section) 138 of the mixer 106 shown in drawing 6, the mixing element 140 which set the head to the axial transportation direction 142 is formed. The filler / processing agent / silicone polymer of a raw material are supplied to the first section 138 of the mixer 106 via the feed hopper 112 shown in drawing 3, and is accelerated and conveyed by the mixing element 140 in the axial transportation direction 142. Drawing 6 shows the pitch of the element heads 122 and 136 seen from the axis formed with the longitudinal direction axis 152 of the mixer shaft 106, and is defined by size drawing 9 of a pitch. The element with not less than 90-degree the helix angle below 180 degrees gives a carrying function, and the element with 0-degree or more the helix angle below 90 degrees gives a retaining function. The mixing element 140 has estranged the mixing element 140 at intervals of about 90 degrees in accordance with the circumference of the shaft 106 as it has extended to near the housing 104 wall so that a dead space may not be produced, and shown in drawing 7.

[0040]The mixing element 140 is set to a transportation direction at an angle of about 138 degrees from perpendicularly it defines as the compass 146 of drawing 9. In accordance with the longitudinal direction axis 150 of a mixer shaft, the vertical axis 152 of the horizontal axis 148 is vertical to the axis 150 at drawing 9. A centrifugal force arises, material is thrown off by rotation of the conveyance element 140, and it becomes an annular form by a radial outer edge of the element 140 by it. Subsequently, an annular feed material will follow mixer 102 inside spirally with a pitch of the element 140.

[0041]The second section 154 of the mixer 102 contains the cutting element 156 which has a pitch with a transportation direction angle of about 118 degrees from a perpendicular. The cutting element 156 is estranged at an angle of about 90 degrees to a circumferencial direction by the shaft 106 circumference as it is shown in drawing 9 with the conveyance element 140, and it has extended to near the wall of the housing 104 so that a dead space may not be produced. The element 156 acts in an operation which separates a conglomerate of material and promotes **** of a filler.

[0042]The third section 158 contains the conveyance element 160 of the reverse pitch in order to

aim at extension of back mixing and holding time.

[0043]According to one embodiment of this invention, the continuation annular layer mixer 102 has at least the first section containing a mixing element, the second section containing a cutting element, and the third section containing a mixing element one by one. This section may be added to an above-mentioned mixing element or cutting element, and may contain other elements. For example, the second section may contain the cutting element and the mixing element. The first section may contain the element of the advance pitch, the second section may contain the front element and the neutral element, and the third section may contain the element of the reverse pitch so that it may increase holding time. The whole element of the continuation annular layer mixer 102. What consists of about 5 – the first section element of 80% of abbreviation, about 10 – the second section element of 85% of abbreviation, and about 0 – the third section element of 75% of abbreviation may be used, May consist of about 10 – the first section element of 65% of abbreviation, about 10 – the second section element of 65% of abbreviation, and about 10 – the third section element of 75% of abbreviation desirably, and, It may consist of about 15 – the first section element of 55% of abbreviation, about 10 – the second section element of 45% of abbreviation, and about 20 – the third section element of 65% of abbreviation preferably.

[0044] The first section 138 where drawing 6 shows one embodiment of this invention, and the continuation annular layer mixer 102 consists of the mixing element 140 of an advance pitch, It has the second section 154 that consists of the cutting element 156 of an advance pitch, and the third section 158 that consists of the mixing element 160 of a reverse pitch one by one. The termination of the mixer 102 is good also as the fourth section 162 that consists of the cutting element 164 of the reverse pitch for discharging a premix, and the following neutral element 168 as shown in drawing 6. The second section 154 may contain the mixing element 166 of the advance pitch.

[0045]In this invention, what unhardened silicone polymer distributed minutely in the filler of the specified quantity is obtained by carrying out preliminary mixing by a continuation annular layer mixer. This material will rank second, and a phase transformation will be carried out under compression and extension / shearing flow field in an extrusion machine, it will be in a compound state, and the dry filler is in a minority group's phase. Mixing time is shortened by eburnation of the filler within an annular layer mixer, and productivity is substantially improved by it.

[0046]These features and the other features will become clear from the following detailed explanation that describes the desirable embodiment of this invention in the sense of illustration, without limiting. In the following embodiments, premix quality is characterized with the particle size in tap density, BET surface area, a solution, and the end of dried powder. A premix material is inspected by the scanning electron microscope, the transmission electron microscope, and a compression test.

[Translation done.]

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EXAMPLE

[Working example] An element of composition of having indicated to Table 1 is provided in an example 1 Drees (Drais)KTT continuation annular layer mixer.

A table 1 element number / explanation angle * theory . ** 1 139 Front conveyance and mixing element . 2 136 front conveyance and mixing element 3. 139 Front conveyance and mixing element 4 135. Front conveyance and mixing element 5 119 Front conveyance / cutting element 6 117 Front conveyance / cutting element 1 122 Front conveyance and mixing element 8 62 Back mixing element 9 68 Back mixing element 10. 71 Back mixing element 11 70 Back mixing element . 12 70 back mixing element 13 69. Back mixing element 14 69 Back mixing element . 15 67 Back mixing element 16 67 Back mixing element 17 124 Front conveyance / cutting element 18 185 An angle from a perpendicular defined by the compass 146 of neutral cutting element * drawing 9 (degree) Use the Doling (Doering) pump (p= 240 psi) for the above-mentioned mixer, and silicone raw rubber is supplied to it at 40 pounds (lbs/hr)/o'clock in speed, Pretreatment fumed silica is supplied at the rate of 60 lbs/hr using a loss-in-quantity type AKURISON (Acrisson) feeder. Any feed is a room temperature. A mixer is operated by 3000 rpm and the amperages 15.5-16.5. Discharging temperature is raised to 81-89 degrees F, and shell temperature is kept at about 73 degrees F. The sample whose tap density is seven, 0.40-0.42, is prepared.

[0048] The Drees mixing stage of Example 1 is repeated using 63 copies of example 2 fumed silica, and 100 copies of polymer crude rubber. Promptly, feed the output of the Drees mixing stage into a Banbury mixer, and Methoxy distal flow object processing agent 2.5 copy, After carrying out compounding to 2.5 copies of a silanol fluid processing agent / processing aid, and 0.8 copy of vinyl methoxysilane cross linking agent, it is made to harden for 10 minutes at 350 degrees F using 1.2 copies of catalysts, and postcure is carried out at 450 degrees F. The physical properties acquired with 75 durometer products are shown in Table 2.

[0049] A filler and polymer are directly put into a Banbury mixer, compounding is carried out to the same material, and it is made to harden like Example 2 for example 3 comparison. The physical properties acquired with 75 durometer products are shown in Table 2.

Table 2 character / example 23 Shore A hardness 72 76 It is extended and is 395, 366 100% modulus 322 355 Tensile 1277 1302 **** B 148 153 Specific gravity 1.226 1.203-example 63 copies of 4 fumed silica, and 100 copies of polymer crude rubber. It uses and the Drees mixing stage of Example 1 is repeated. The output of the Drees mixing stage is promptly fed into a Banbury mixer, and compounding is carried out to methoxy distal flow object processing agent 2.5 copy, 2.5 copies of silanol fluid processing agents / processing aid, and 0.8 copy of vinyl methoxysilane cross linking agent. Compounding of the sample which consists of such materials is carried out with the Banbury mixer of various RPM. The sample which carried out compounding is stiffened for 12 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the obtained sheet-shaped sample is carried out at 200 ** for 4 hours. The physical properties over 75 durometer sample are shown in Table 3.

A table 3 character / example RPM1400200028003200 Shore A hardness 76 77 75 75 It is extended and is 324. 347 308 323 100% modulus 410 407 385 366 Tensile 1327 1398. 1210 1220 *** B 134 126 126 130 Specific gravity 1.207 1.209 1.198 The Drees mixing stage of Example 1 is repeated using 1.199—example 63 copies of 5 fumed silica, and 100 copies of polymer crude rubber. After feeding output of the Drees mixing stage into the geared type said direction rotation twin screw extruder continuously and carrying out compounding to it, it supplies to a both-way formula single screw extruder continuously, and uniformity and stripping are performed. An ultimate product includes three copies of sources of methylvinyl as 1.35 copies of vinylidol cross linking agents, 2.0 copies of silanol fluid processing agents / processing aid, and a cross linking agent/plasticizer. Output is volatile-matter-content <1%. Output is stiffened for 17 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the product sheet is carried out at 200 ** for 4 hours. Physical properties in 75 durometer sample are shown in Table 4.

[0050]The Drees mixing stage of Example 1 is repeated using 61 copies of example 6 fumed silica, and 100 copies of polymer crude rubber. After feeding the output of the Drees mixing stage into the geared type said direction rotation twin screw extruder continuously and carrying out compounding to it, it supplies to a non-engagement type different direction rotation twin screw extruder continuously, and uniformity and stripping are performed. The ultimate product includes 0.5 copy of source of methylvinyl as 1.0 copy of a silanol fluid processing agent / processing aid, and a cross linking agent/plasticizer. Output is volatile-matter-content <1%. Output is stiffened for 17 minutes at 260 degrees F by 1.5 copies of 2,4-dichlorobenzyl peroxide. Postcure of the product sheet is carried out at 200 ** for 4 hours. The physical properties in 40 durometer sample are shown in Table 4.

a table — 4 character / example 56 Shore A hardness 70.1 being extended 37.8 — 327 519 100% modulus 420 108 tension 1467 1078 *** B 123 69 specific-gravity 1.21 1.106 — as the result of these shows, If a premix is prepared continuously in a high-speed mixing stage, a free fluid granular concentrate is formed and it supplies to compounding equipment continuously, a thermosetting silicone composition can be prepared.

[0051]Although the desirable embodiment of this invention has been described, change and correction are possible for this invention, and it is not limited to the details of an embodiment. This invention includes the change and change belonging to Claims.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a schematic view of the continuation thermosetting silicone composition compounding method and equipment.

[Drawing 2] It is a schematic view of the continuation thermosetting silicone composition compounding method and equipment.

[Drawing 3] It is a side elevational view of a continuation annular layer mixer.

[Drawing 4] It is a perspective diagram of a mixer element.

[Drawing 5] It is a perspective diagram of a mixer element.

[Drawing 6] It is an approximate account figure of an element and the pitch of the element is shown.

[Drawing 7] It is the approximate account figure seen through the A-A line of drawing 3.

[Drawing 8] It is the approximate account figure seen through the B-B line of drawing 3.

[Drawing 9] It is the standard compass for determining the pitch of an element.

[Explanations of letters or numerals]

12 High-speed mixing stage

14 Extrusion machine stage

16 and 60 Loss-in-quantity feeder

20 Silicone polymer

22 and 66 Processing agent

24 and 70 Free mobility premix

26 Additive agent

30 and 80 Thermosetting silicone polymer constituent

52 Continuation annular layer high speed mixer

54 The second mixer

56 and 58 Extrusion machine

62 Filler

102 Continuation annular layer mixer

104 Cylindrical housing

106 Central lengthwise direction shaft

112 Material supply port

114 Outlet

116,140 mixing elements

118,128 Stem

122 End sector head

124,156 Cutting element

134 Cutting edge

138 Supply (first) section

142 Shaft-orientations transportation direction

- 154 The second section
- 158 The third section
- 160 The conveyance element of a reverse pitch
- 162 The fourth section
- 164 The cutting element of a reverse pitch
- 166 The mixing element of an advance pitch
- 168 Neutral element

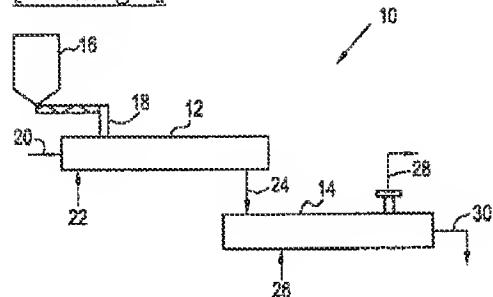
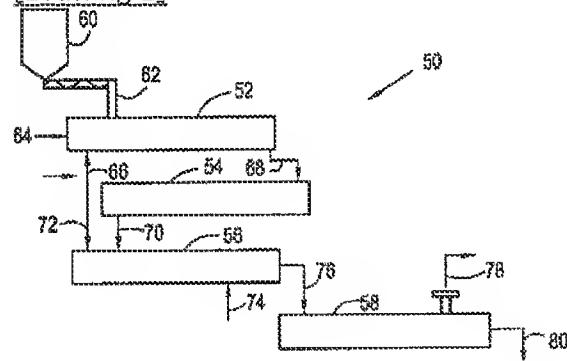
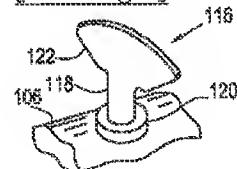
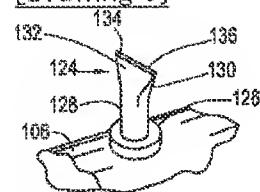
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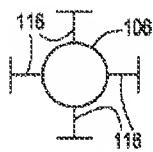
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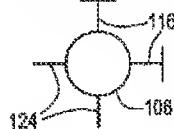
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DRAWINGS

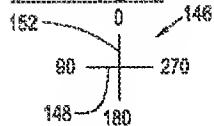
[Drawing 1]**[Drawing 2]****[Drawing 4]****[Drawing 5]****[Drawing 7]**



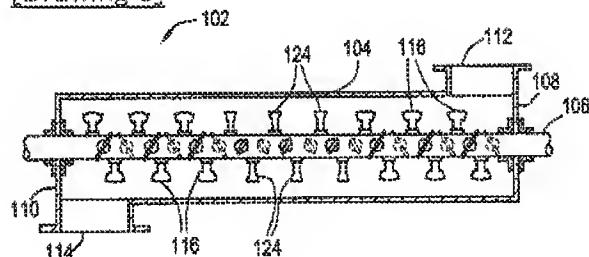
[Drawing 8]



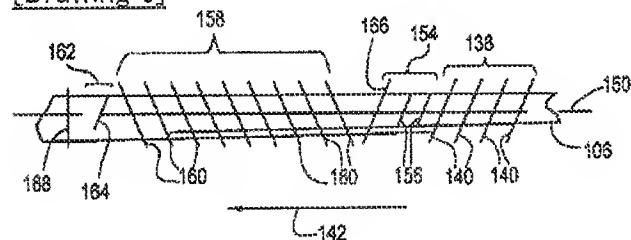
[Drawing 9]



[Drawing 3]



[Drawing 6]



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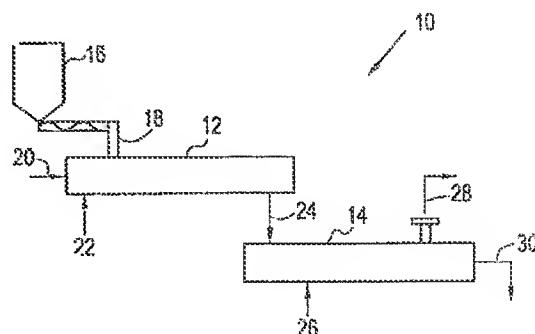
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(54)【発明の名称】熱硬化性シリコーン組成物の連続製造法

(57)【要約】

【課題】高レベルの充填材、加工流体及びシリコーンポリマーをコンパウンドィングして所要の補強特性と揮発分レベルを有する均一な充填材配合熱硬化性シリコーン組成物を得る方法の提供。

【解決手段】高レベルの処理ヒュームドシリカ、加工流体及び高分子量シリコーンポリマーを連続的にコンパウンドィングして均一なシリカ充填熱硬化性シリコーン組成物とするために、連続環状層ミキサー内でプレミックスを形成し、そのプレミックスをコンパウンドィング装置に連続的に排出しコンパウンドィングして充填材配合熱硬化性シリコーン組成物を形成する。



【特許請求の範囲】

【請求項1】 充填材配合熱硬化性シリコーン組成物のコンパウンドィング方法であって、当該方法が、充填材とシリコーンポリマーを高速混合段に連続的に供給して自由流動性の粒状コンセントレートを形成し、上記自由流動性粒状コンセントレートを混合段からコンパウンドィング装置に連続的に排出することを含んでなる方法。

【請求項2】 前記コンセントレートを前記コンパウンドィング装置内で連続的にコンパウンドィングして充填材配合熱硬化性シリコーン組成物を形成することを含んでなる、請求項1記載の方法。

【請求項3】 前記混合段が剪断及び攪拌機構からなる、請求項1記載の方法。

【請求項4】 前記混合段が連続環状層ミキサーを含んでなる、請求項1記載の方法。

【請求項5】 前記コンパウンドィング装置が螺旋駆動押出機構である、請求項1記載の方法。

【請求項6】 前記混合段が直列に接続した2つの連続環状ミキサーを含んでなり、連続環状層ミキサー中で充填材をシリコーンポリマーと約5秒～約10分の滞留時間で混合してプレミックスを形成し、プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項1記載の方法。

【請求項7】 前記混合段が直列に接続した2以上の連続環状ミキサーを含んでなり、連続環状層ミキサー中で充填材をシリコーンポリマーと約10秒～約5分の滞留時間で混合してプレミックスを形成し、プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項1記載の方法。

【請求項8】 前記混合段が直列に接続した2つの連続環状ミキサーを含んでなり、連続環状層ミキサー中で充填材をシリコーンポリマーと約20秒～約3分の滞留時間で混合してプレミックスを形成し、プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項1記載の方法。

【請求項9】 前記混合段が連続環状層ミキサーであり、前記コンパウンドィング装置が螺旋駆動押出機構である、請求項1記載の方法。

【請求項10】 前記連続環状層ミキサーが前記コンパウンドィング装置に隣接して接続されている、請求項9記載の方法。

【請求項11】 前記連続環状層ミキサーが前記コンパウンドィング装置に接して接続されている、請求項9記載の方法。

【請求項12】 前記連続環状層ミキサー中で約3～約100m/sのエレメント先端速度で充填材をシリコーンポリマーと混合してプレミックスを形成し、

プレミックスをコンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項13】 前記連続環状層ミキサー中で約10～約80m/sのエレメント先端速度で充填材をシリコーンポリマーと混合してプレミックスを形成し、

プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項14】 前記連続環状層ミキサー中で約15～約60m/sのエレメント先端速度で充填材をシリコーンポリマーと混合してプレミックスを形成し、

プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項15】 前記連続環状層ミキサー中で充填材をシリコーンポリマーと約3秒～約5分の滞留時間で混合してプレミックスを形成し、

プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項16】 前記連続環状層ミキサー中で充填材をシリコーンポリマーと約5秒～約1分の滞留時間で混合してプレミックスを形成し、

プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項17】 前記連続環状層ミキサー中で充填材をシリコーンポリマーと約20～約45秒の滞留時間で混合してプレミックスを形成し、

プレミックスを前記コンパウンドィング装置に排出することを含んでなる、請求項9記載の方法。

【請求項18】 前記連続環状層ミキサーが、少なくとも、混合エレメントを含む第一セクションと切断エレメントを含む第二セクションと混合エレメントを含む第三セクションとを順次有する、請求項9記載の方法。

【請求項19】 前記連続環状層ミキサーが、少なくとも、前進ピッチの混合エレメントを含む第一セクションと前進ピッチの切断エレメント又はニュートラル切断エレメントを含む第二セクションと後進ピッチの混合エレメントを含む第三セクションとを順次有する、請求項9記載の方法。

【請求項20】 前記連続環状層ミキサーが、約5～約80%の第一セクションエレメントと約10～約85%の第二セクションエレメントと約0～約75%の第三セクションエレメントとを含んでなる、請求項19記載の方法。

【請求項21】 前記連続環状層ミキサーが、約10～約65%の第一セクションエレメントと約10～約65%の第二セクションエレメントと約10～約75%の第三セクションエレメントとを含んでなる、請求項19記載の方法。

【請求項22】 前記連続環状層ミキサーが、約15～約55%の第一セクションエレメントと約10～約45

%の第二セクションエレメントと約20～約65%の第三セクションエレメントとを含んでなる、請求項19記載の方法。

【請求項23】 前記連続環状層ミキサーが、前進ピッチの切断エレメント又は前進ピッチの混合エレメントを含む最終セクションもさらに含んでいる、請求項19記載の方法。

【請求項24】 充填材配合熱硬化性シリコーン組成物のコンパウンドィング方法であって、当該方法が、連続環状層ミキサー中に約3～約100m/sのエレメント先端速度で充填材をシリコーンポリマーと混合してプレミックスを形成し、プレミックスを次の加工装置に排出することを含んでなる方法。

【請求項25】 前記先端速度が約10～約80m/sである、請求項24記載の方法。

【請求項26】 前記先端速度が約15～約80m/sである、請求項24記載の方法。

【請求項27】 充填材配合熱硬化性シリコーン組成物製造用のプレミックスを形成する方法であって、当該方法が、連続環状層ミキサー中に充填材をシリコーンポリマーと混合し、充填材配合シリコーンポリマー/プレミックスをミキサーから排出することを含んでなる方法。

【請求項28】 前記プレミックスを貯蔵区域に排出する、請求項27記載の方法。

【請求項29】 前記プレミックスを排出し、さらに加工するための区域に輸送する、請求項27記載の方法。

【請求項30】 前記プレミックスを排出し、さらに加工するための区域に輸送する、請求項27記載の方法。

【請求項31】 少なくとも、混合エレメントを含む第一セクションと切断エレメントを含む第二セクションと混合エレメントを含む第三セクションとを順次含んでなる、連続環状層ミキサー。

【請求項32】 少なくとも、前進ピッチの混合エレメントを含む第一セクションと前進ピッチの切断エレメント又はニュートラル切断エレメントを含む第二セクションと後進ピッチの混合エレメントを含む第三セクションとを順次含んでなる、請求項31記載の連続環状層ミキサー。

【請求項33】 約5～約80%の第一セクションエレメントと約10～約85%の第二セクションエレメントと約0～約75%の第三セクションエレメントとを含んでなる、請求項31記載の連続環状層ミキサー。

【請求項34】 約10～約65%の第一セクションエレメントと約10～約65%の第二セクションエレメントと約10～約75%の第三セクションエレメントとを含んでなる、請求項31記載の連続環状層ミキサー。

【請求項35】 約15～約55%の第一セクションエ

レメントと約10～約45%の第二セクションエレメントと約20～約65%の第三セクションエレメントとを含んでなる、請求項31記載の連続環状層ミキサー。

【請求項36】 前進ピッチの切断エレメント又は前進ピッチの混合エレメントを含む最終セクションもさらに含んでいる、請求項31記載の連続環状層ミキサー。

【請求項37】 第一段の連続環状層ミキサーと、加工材料を第一段から第二段に連続的に排出できるように第一段と接続した押出機を含む1以上の後段とを含んでなるコンパウンドィング装置。

【請求項38】 第一段の連続環状ミキサーが、少なくとも、混合エレメントを含む第一セクションと切断エレメントを含む第二セクションと混合エレメントを含む第三セクションとを順次有する、請求項37記載のコンパウンドィング装置。

【請求項39】 第一段の連続環状ミキサーが、少なくとも、前進ピッチの混合エレメントを含む第一セクションと前進ピッチの切断エレメント又はニュートラル切断エレメントを含む第二セクションと後進ピッチの混合エレメントを含む第三セクションとを順次有する、請求項37記載のコンパウンドィング装置。

【請求項40】 第一段の連続環状ミキサーが、約5～約80%の第一セクションエレメントと約10～約85%の第二セクションエレメントと約0～約75%の第三セクションエレメントとを含んでなる、請求項37記載のコンパウンドィング装置。

【請求項41】 第一段の連続環状ミキサーが、約10～約65%の第一セクションエレメントと約10～約65%の第二セクションエレメントと約10～約75%の第三セクションエレメントとを含んでなる、請求項37記載のコンパウンドィング装置。

【請求項42】 第一段の連続環状ミキサーが、約15～約55%の第一セクションエレメントと約10～約45%の第二セクションエレメントと約20～約65%の第三セクションエレメントとを含んでなる、請求項37記載のコンパウンドィング装置。

【請求項43】 第一段の連続環状ミキサーが、前進ピッチの切断エレメント又は前進ピッチの混合エレメントを含む最終セクションもさらに含んでいる、請求項37記載のコンパウンドィング装置。

【請求項44】 前記混合エレメントがステムを含んでいてその終端の遠位扇形ヘッドまで延在しており、前記切断エレメントがステムを含んでいてその遠位ヘッドで外側に聞くとともに内側に面取りされて切刃をなす、請求項38記載のコンパウンドィング装置。

【請求項45】 前記第二段が噛合型同方向回転二軸押出機を含んでいる、請求項37記載のコンパウンドィング装置。

【請求項46】 前記第二段が非噛合型同方向回転二軸押出機を含んでいる、請求項37記載のコンパウンドィ

ング装置。

【請求項47】 前記段が別個の隣接する段である、請求項37記載のコンパウンディング装置。

【請求項48】 前記段が連続して接する段である、請求項37記載のコンパウンディング装置。

【請求項49】 第一段が直列に配置した複数のミキサーを含んでいる、請求項37記載のコンパウンディング装置。

【請求項50】 第一段が複数のミキサーを含んでおり、2以上のミキサーがタンデムに作動するように配置されている、請求項37記載のコンパウンディング装置。

【請求項51】 前記1以上の後段が噛合型同方向回転二軸押出機、異方向回転二軸押出機、又は単軸押出機からなる、請求項37記載のコンパウンディング装置。

【請求項52】 前記1以上の後段が噛合型同方向回転二軸押出機又は往復式単軸押出機からなる、請求項37記載のコンパウンディング装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は熱硬化性シリコーン組成物を連続的に製造する方法に関する。

【0002】

【従来の技術】 热硬化性シリコーン組成物は、高粘度シリコーンポリマー、補強用無機充填材及び加工助剤その他組成物に所望の最終特性を与える各種添加剤を含んでいる。加硫剤を添加して組成物を熱硬化すれば、ガスケット、医療用チューブ及びコンピューターキーパッドのようなシリコーンゴム成形品を製造することができる。

【0003】 热硬化性シリコーン組成物は、通常、高粘度ポリジオルガノシロキサン、無機充填材及び添加剤を高強度バンパリーミキサー又は低強度双腕型ドウミキサーのようなバッチ式混練機で混練することによって製造される。この方法では、ポリジオルガノシロキサン、無機充填材、処理剤及び添加剤を所望の特性が得られるまでバッチ方式で混合する。Kasahara他の米国特許第5198171号では、ポリジオルガノシロキサン、無機充填材及び処理剤のプレコンセントレートを高速の機械的剪断ミキサーで形成する。得られたプレミックスを同方向回転二軸押出機さらにコンパウンディングする。プレミックスは、25°Cで 1×10^5 cP以上の粘度を有するジオルガノポリシロキサン、無機充填材及び処理剤を高速機械剪断機で混合して各成分が実質的に均一な微細分散状態で存在する流動性粒状混合物を提供する第一段で形成される。流動性粒状混合物を、次いで同方向回転二軸混練押出機に一定の供給速度で供給する。

【0004】 バッチ式プロセスには長い混合時間と大量のエネルギーが必要とされる。工業規模のバッチ全体では剪断・伸長応力が不均一となって充填材の粒度分布が

不均一となって、特性にバラツキを生じかねない。異なる時期に加工されたバッチは物性が種々異なる可能性がある。バッチプロセスは労力・エネルギー・資本を大量に消費し、しかも単に限界ぎりぎりのコンシステンシーの物質を生じるに過ぎない。

【0005】 Hamada他の米国特許第5409978号では、同方向回転二軸連続押出機でポリジオルガノシロキサン、無機充填材及び処理剤のプレコンセントレートを約200～300°Cの温度で形成する。プレコンセントレートを次いで異方向回転二軸押出機でコンパウンディングして150～300°Cで熱処理する。ただし、2つの押出機を要するプロセスは高価であり、しかも大きな作業面積を必要とする。

【0006】

【発明が解決しようとする課題】 しかし、これらの方では処理量が限られている。向上した処理量を与えるとともに、単一の押出機を効率的に利用して充填材と添加剤とポリマーから低粘度乃至高粘度の全域にわたるシリコーンエラストマーを連続的に一貫して生産できる低コストプロセスとして適合させることができる方法が必要とされている。

【0007】

【課題を解決するための手段】 本発明は、高レベルの充填材、加工流体及びシリコーンポリマーをコンパウンディングして所要の補強特性と揮発分レベルを有する均一な充填材配合熱硬化性シリコーン組成物を得る方法を提供する。この方法では、充填材とシリコーンポリマーを高速混合段に連続的に供給して自由流動性の粒状コンセントレートを形成する。このコンセントレートを混合段からコンパウンディング装置に連続的に排出してさらに加工処理する。

【0008】 別の態様では本発明は、充填材とシリコーンポリマーのプレミックスを形成する方法に関する。この方法では、連続環状層ミキサーで充填材をシリコーンポリマーと混合し、この充填材配合シリコーンポリマープレミックスをミキサーから排出する。

【0009】 別の態様では本発明は充填材配合熱硬化性シリコーン組成物をコンパウンディングする方法に関する。この方法では、高速連続ミキサー内で約3～約100m/sのエレメント先端速度で充填材をシリコーンポリマーと混合する。次にこのプレミックスを次の加工処理装置に排出する。

【0010】 別の態様では本発明は、少なくとも、前進ピッチの混合エレメントを含む第一セクションとニュートラル又は前進ピッチの切断エレメントを含む第二セクションと後進ピッチの混合エレメントを含む第三セクションとを順次有する連続環状層ミキサーに関する。

【0011】 さらに別の態様では本発明は、第一段の連続環状層ミキサーと、加工材料を第一段から第二段に連続的に排出できるように第一段と接続した押出機を含む

以上の後段とを含んでなるコンパウンドィング装置に関する。

【0012】

【発明の実施の形態】充填材とシリコーンポリマーのバッチ式コンパウンドィング用としてパンパリー・ミキサー又はドウミキサーが知られている。このコンパウンドィング作業は2つの別個の段階があり、第一段階では充填材をポリマーで温らし、第二段階では凝集塊を細かく破碎して充填材をポリマー中に均一に分散させる。充填材がポリマーに十分に分散することが重要である。分散していない大きな凝集塊は、破壊を引き起こす欠陥として作用しかねないので機械的特性に劣ることになる。

【0013】バッチ式又は連続式プロセスでは、充填材の添加時又は添加前に処理剤をシリコーンポリマーと一緒に分散させることができる。これらのプロセスでは、シリコーンポリマーと充填材に存在する遊離の未反応シラノール基との間に大きな界面力が発生する。処理のため、処理剤は大量の高分子量シリコーンポリマーに拡散して、硬直したシリコーンポリマー/充填材界面に浸透して充填材に達しなければならない。処理剤が浸透してシラノール基に接近するには大きな界面力に打ち勝つように混合強度を増す必要がある。混合強度の増大は不都合な材料温度の上昇を引き起す。

【0014】本発明では、シリコーンと充填材の自由流動性の粒状コンセントレートを高速混合段で連続的に形成する。このコンセントレートをさらに加工処理するため混合段からコンパウンドィング装置に連続的に排出する。混合段は連続環状層ミキサーからなるものとし得る。連続環状層ミキサーは円筒形混合トラフを含んでおり、混合材料は円筒形ミキサー壁と接触して環状にトラフ軸に沿って螺旋経路を進む。典型的な連続環状層ミキサーはE·r·i·c他の米国特許第5,018,673号に開示されている。この米国特許には、実質的に水平に配置された円筒形ハウジングを含むミキサーが記載されており、ハウジングの第一の端には材料を連続的に供給するための材料供給管が設けられ、その第二の端には材料を連続的に取り出すための材料排出管が設けられている。円筒形ハウジングは、該ハウジング内に同軸に配置された混合装置を囲んでいる。混合装置は高速で駆動し得る。この装置は混合具を含んでおり、混合具は装置からハウジング内壁近くまで略半径方向に突出している。このミキサーは材料供給管とつながる供給ゾーンと、供給ゾーンの軸方向の搬送方向下流に設けられた加湿ゾーンとを含んでいる。このミキサーには、液体を環状材料中に進入させるための手段が加湿ゾーンに設けられている。環状材料はハウジング内壁上でミキサー内を螺旋状に搬送され、移動する。ミキサーは集塊分離手段をさらに含んでいる。この手段は、混合装置のシャフトに対して半径方向平面内に設けられた切断具で、ハウジングの全周にわたって等間隔に配置された複数の切断具を含ん

でいる。

【0015】本発明の一つの実施形態では、連続環状層ミキサーを予備混合段として用いて、所定量の充填材中で未硬化シリコーンポリマーの微細分散体を形成する。この材料は次いで押出機内の圧縮・伸長・剪断流れ場の下で相変態してコンパウンド状態となり、乾いた充填材は少數派の相にある。第一段での緻密化によって押出機内の混合時間が短縮化され、生産性が大幅に改善される。

【0016】本発明で使用し得る無機充填材は、シリコーンポリマーとのブレンドに使用される無機充填材であればどんなものでもよい。無機充填材の例には、ヒュームドシリカや沈降シリカのような補強用シリカ、或いはオルガノポリシロキサン、オルガノアルコキシラン、オルガノクロロシラン又はヘキサオルガノジシラザンのような有機ケイ素化合物で表面処理したシリカがある。充填材はケイ藻土、微粉碎石英、酸化アルミニウム、酸化チタン、酸化鉄、酸化セリウム、水酸化セリウム、酸化マグネシウム、酸化亜鉛、炭酸カルシウム、ケイ酸ジルコニウム、カーボンブラック又は滑石であってよい。シリコーンポリマーを補強するため、單一種の充填材又は充填材の組合せを使用し得る。

【0017】充填材の量は、シリコーンポリマー100重量部当たり、約5~約200重量部、望ましくは約10~約100重量部、好ましくは約20~約60重量部とし得る。

【0018】充填材表面の残留シラノール基は、シリカとシリコーンポリマー鎖のヒドロキシル基又は酸素基との水素結合の強度を支配する可能性がある。充填材に高濃度の残留シラノールが存在すると貯蔵時に最終製品の「ストラクチャ形成」又は「クレープ硬化」を引き起す。この効果は、長期間貯蔵した後の材料の加工を困難にする。充填材のシラノール官能基の濃度が高過ぎる場合、処理剤の添加によりシラノール基を所要濃度まで下げることができる。シラノール反応体処理剤は有効基と反応して濃度を充填材の単位面積(平方ナノメートル)当たりヒドロキシル基約8~約2個、好ましくは約7~約3個に下げることができる。表面処理シリカが本発明において好ましい充填材であり、その量はシリコーンポリマー100重量部当たり約10~約100重量部、好ましくは約20~約60重量部である。

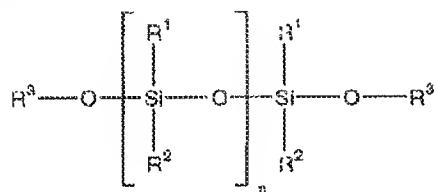
【0019】処理剤を充填材に混合すれば、充填材のシラノール基を低減し、充填材の分散性を改善及び/又はシリコーンゴムのエージングに必要な時間を短縮し、クレープ硬化を防止及び/又は可塑性を調節することができる。処理剤はオルガノシラン、低粘度ポリシロキサン又はシリコーン樹脂と/orでき、シラノール基及び/又は炭素原子数1~6のアルコキシ基を有する。例として、ジフェニルシランジオール、ジメチルシランジオール、メチルトリエトキシシラン及びフェニルトリ

メトキシシランがある。低粘度ポリシロキサンはメチル基、フェニル基、ビニル基及び3, 3, 3-トリフォルオロブロビル基から選択される1種類以上の有機基を含んでいてもよい。25°Cで測定したポリシロキサンの粘度は約1～約300cP、好ましくは約5～約100cPである。処理剤は、充填材100重量部当たり0、1～100重量部、望ましくは0、5～約50重量部、好ましくは約1、0～約20重量部の量で添加し得る。好ましいシラノール反応体処理剤としては、シラノール末端ポリジメチルシロキサン、オクタメチルシクロテトラシロキサン(D4)及びヘキサメチルジシラザン(HMDZ)がある。

【0020】本発明の組成物に用いられるシリコーンポリマーは次の式Iの繰返し単位で表すことができる。

【0021】

【化1】



式 I

【0022】式中、R¹は各々独立にC₁₋₄アルキル又はC₂₋₄アルキレンを表し、R²は各々独立にC₁₋₄アルキル、C₁₋₄ハロアルキル又はC₂₋₄アルキレンを表し、R³は各々独立にH、C₁₋₁₀アルキル、C₂₋₄アルキレン、C₄₋₆シクロアルキル、OH又はC₁₋₄ハロアルキルを表し、nは1000～20000の整数を表す。

【0023】さらに好ましい組成物は、R¹が各々独立にCH₃又はCH=CH₂を表し、R²が各々独立にCH₃、CH=CH₂又はCH₂CH₂CF₃を表し、R³が各々独立にCH₃、CH=CH₂、OH又はCH₂CH₂CF₃を表し、nが約4000～約10000の整数を表すシリコーンポリマーを含む。

【0024】別の実施形態では、シリコーンポリマーのビニル含量がシリコーンポリマーの約0、05～約0、5重量%である組成物が提供される。

【0025】熱硬化性シリコーン組成物は、金属の酸化物、水酸化物及び脂肪酸塩のような耐熱性向上剤、加硫戻り防止剤、白金化合物のような難燃剤、変色防止剤、シリコーンオイルのような可塑剤、金属石鹼のような内部離型剤、顔料並びに染料のような他の添加剤を含んでいてもよい。

【0026】本発明の特徴は添付の図面と以下の詳細な説明から明らかとなるが、これらは本発明の実施形態を例示するためのもので本発明を限定するものではない。

【0027】図1は、本発明の方法の概略を示す。

【0028】図1で、本発明の装置は高速混合段12と押出機段14を含んでいる。高速混合段12は連続環状層ミキサーでもよいし、また単一のミキサーであっても直列に配置した複数のミキサーであってもよい。押出機段14は、噛合型同方向回転二軸押出機、異方向回転二軸押出機又は単軸押出機の1以上とすることができる。好ましくは、押出機段14は噛合型同方向回転二軸押出機又は往復式単軸押出機である。押出機段が複数の押出機を含んでいる場合には、直列又はタンデムに接続し得る。

【0029】本発明の方法では、充填材は減量フィーダー16に収容され、シリコーンポリマー20及び処理剤22と共に18で混合段12に供給される。

【0030】混合段12では、ポリマー、充填材及び処理剤は高速で強力な力に付され、自由流動性の粉末プレミックス24を生じる。材料を細かく粉碎し、充填材をポリマーで被覆するとともに材料を処理剤で濡らすため、適当な先端速度と滞留時間が必要とされる。プレミックスを形成するには、材料を約3～約100m/sのエレメント先端速度で混合すればよい。望ましくは、エレメント先端速度は約1.0～約8.0m/s、好ましくは約1.5～約6.0m/sである。滞留時間は材料がミキサーを通過するのに要する時間である。単一のミキサーを用いる場合、滞留時間は約3秒～約5分(min)とし得る。単一のミキサーについての滞留時間は約5s～約1min、好ましくは約20s～約45sとし得る。混合段12は複数のミキサーを含んでいてもよい。2つのミキサーを直列に使用する場合、2台についての滞留時間は約5s～約10minであってもよいし、或いは滞留時間は約10s～約5min、好ましくは20s～約3minとし得る。混合段12では、タップ密度約0、3～約0、6、又は約0、35～約0、55、さらには0、36～約0、48の生成物を生じ得る。

【0031】好都合なことに、プレミックス24は(図示したように)連続法で使用することもできるし、或いは後で使用するために貯蔵分配してもよい。図1でプレミックス24は押出機段14に供給され、そこで添加剤26とコンパウンドングされ、揮発分が除かれて、熱硬化性シリコーンポリマー組成物30を生じる。

【0032】図2に、本発明の別の実施形態を示す。図2の装置50は連続環状層高速ミキサー52と直列に配置された第二のミキサー54とを含んでいる。滞留時間を延ばしてバラツキの少ないプレミックスを得るため、2台以上のミキサーを利用してもよい。図2の装置は、ミキサー52、54の下流で直列に接続した押出機56と押出機58を含んでいる。

【0033】図2に示す方法では、減量フィーダー60で充填材62を秤量して第一のミキサー52に入れてポリマー62及び処理剤64と混合する。ミキサー52の

生成物をミキサー4に68で供給し、そこで自由流動性の粉末プレミックス70が生じる。それを押出機56に供給し、そこでさらに充填材処理するために追加の処理剤を72で加える。低ジュロメーター材料を製造するため、この段階で追加のポリマー（図示せず）を加えてよい。この段階で加工助剤その他の添加剤を74で加えて生成物76を得て、それを押出機58に供給して78で揮発分を除く。押出機58で熱硬化性シリコーンポリマー組成物80が得られるので、それを使用すればよい。

【0034】図3～図8に、連続環状層ミキサーと付属エレメントを示す。

【0035】図4及び図5に、本発明で使用し得るミキサーに装備し得る加工エレメントを示す。図3は、図4及び図5のエレメントの配置を示す連続環状層ミキサー102の側面立面図である。

【0036】図3で、ミキサー102は中心に長手方向シャフト106を有する円筒形ハウジング104を含んでいる。ハウジング104は両端が端壁108, 110で封止されている。シャフト106はハウジング104の両端を貫通して突き出しており、端壁108, 110で封止されている。ハウジング104の上部には原料供給口112が取り付けられていてハウジング104内部に向かって略接線方向に開いており、ハウジング104の下端にはハウジング104の内部に向かって略接線方向に排出口114が備えられていてハウジング104の内部から開放されている。

【0037】様々な設計の加工エレメントがミキサー102のシャフト106に設けられる。図4は、回転シャフト106から延在し、図3の連続環状層ミキサー102内でシャフト106から半径方向に突き出ている混合エレメント116を示す。混合エレメント116はシャフト106つまり長手方向軸に見て、図7及び図8に示す通り軸方向に90°間隔で整列している。混合エレメント116はベース120から終端の遠位頭形ヘッド122まで延在するシステム118を含んでいる。図示した混合エレメント116は、ベース120に対して垂直に延在し、角度の付いたバドルヘッド122をもつ。エレメント116は、場合に応じて、搬送（推進）機能又は逆混合機能を比較的増すため所定のヘッドピッチ角でベース120に固定される。エレメントの様々なピッチと機能の説明は後で図6～図9を参照して説明する。

【0038】図5に、ベース126から延在し、ミキサー102内でシャフト106から半径方向に延びる切断エレメント124を示す。切断エレメント124は、システム128を含んでいてその遠位ヘッド136で外側に開く（130）とともに内側に面取り（132）されて刃134をなす。図示したエレメント124は、垂直に延在している。エレメント124は、図6～図9を参照して説明するように搬送機能及び逆混合機能を調節す

るため所定の切断エッジピッチ角で固定し得る。エレメント124はシャフト106つまり長手方向軸に見て、図8に示す通り軸方向に90°間隔で整列している。

【0039】図6はエレメントの概略説明図であり、ミキサー・シャフト106に関するエレメントのピッチを示している。図6に示すミキサー106の第一の供給セクション（第一セクション）138では、ヘッドを軸搬送方向142にセットした混合エレメント140が設けられている。原料の充填材/処理剤/シリコーンポリマーは図3に示す供給口112を介してミキサー106の第一セクション138に供給され、混合エレメント140で軸搬送方向142に加速され搬送される。図6は、ミキサー・シャフト106の長手方向軸152で画成される軸からみたエレメントヘッド122及び136のピッチを示しており、ピッチの大きさ図9で定義される。90°以上180°未満のピッチ角をもつエレメントは搬送機能を与え、0°以上90°未満のピッチ角をもつエレメントは保持機能を与える。混合エレメント140はデッドスペースを生じないようにハウジング104内壁近傍まで延在しており、また、図7に示す通り混合エレメント140はシャフト106の円周に沿って約90°間隔で離間している。

【0040】混合エレメント140は図9のコンパス146で定義される垂直方向から約138°の角度で搬送方向にセットされている。図9で、横軸148はミキサー・シャフトの長手方向軸150と一致し、縦軸152は軸150に垂直である。搬送エレメント140の回転によって遠心力が生じて、材料が投げ飛ばされエレメント140の半径方向外端で環状の形態となる。次いで、エレメント140のピッチによって環状の供給材料がミキサー102内部を螺旋状に進むことになる。

【0041】ミキサー102の第二セクション154は、垂直から約118°の搬送方向角のピッチをもつ切断エレメント156を含んでいる。切断エレメント156は、図9に搬送エレメント140と共に示す通りシャフト106周囲で円周方向に約90°の角度で離間しており、デッドスペースを生じないようにハウジング104の内壁近傍まで延在している。エレメント156は材料の集塊を分離して充填材の漏れを促進する作用を果たす。

【0042】第三セクション158は、逆混合及び滞留時間の延長を図るため後進ピッチの搬送エレメント160を含んでいる。

【0043】本発明の一つの実施形態では、連続環状層ミキサー102は、少なくとも、混合エレメントを含む第一セクションと切断エレメントを含む第二セクションと混合エレメントを含む第三セクションとを順次有する。かかるセクションは上記の混合エレメント又は切断エレメントに加えて他のエレメントを含んでいてよい。例えば、第二セクションは切断エレメントと混合エ

レメントを含んでいてもよい。第一セクションは前進ピッチのエレメントを含んでいてもよく、第二セクションは前方エレメントとニュートラルエレメントを含んでいてもよく、第三セクションは滞留時間を増大させるべく後進ピッチのエレメントを含んでいてもよい。連続環状層ミキサー102のエレメント全体は、約5～約80%の第一セクションエレメントと約10～約85%の第二セクションエレメントと約0～約75%の第三セクションエレメントからなるものでよく、望ましくは約10～約65%の第一セクションエレメントと約10～約65%の第二セクションエレメントと約10～約75%の第三セクションエレメントとからなるものでもよいし、好ましくは約15～約55%の第一セクションエレメントと約10～約45%の第二セクションエレメントと約20～約65%の第三セクションエレメントとからなるものでよい。

【0044】図6は本発明の一つの実施形態を示しており、連続環状層ミキサー102は前進ピッチの混合エレメント140からなる第一セクション138と、前進ピッチの切断エレメント156からなる第二セクション154と、後進ピッチの混合エレメント160からなる第三セクション158とを順次有している。図6に示す通り、ミキサー102の終端は、プレミックスを排出する

ための後進ピッチの切断エレメント164と後続のニュートラルエレメント168とからなる第四のセクション162としてもよい。また、第二セクション154は前進ピッチの混合エレメント166を含んでいてもよい。

【0045】本発明では、連続環状層ミキサーで予備混合することにより、所定量の充填材中に未硬化シリコーンポリマーが微細に分散したものが得られる。この材料は次いで押出機内の圧縮・伸長・剪断流れ場の下で相変態してコンパウンド状態となり、乾いた充填材は少數派の相にある。環状層ミキサー内での充填材の緻密化によって混合時間が短縮され、生産性が大幅に改善される。

【0046】これらの特徴及びその他の特徴は、限定することなく例示の意味で本発明の好ましい実施形態を説明する以下の詳細な説明から明らかとなろう。以下の実施例で、プレミックスの品質はタップ密度、BET表面積、溶液及び乾燥粉末の粒度で特徴付ける。プレミックス材料は走査型電子顕微鏡、透過型電子顕微鏡及び圧縮試験で検査する。

【0047】

【実施例】例1

ドレイス(Draiss) KTT連続環状層ミキサーに、表1に記載した構成のエレメントを設ける。

表 1

エレメント	番号/説明	角度*	説明
1	139	前進搬送・混合エレメント	
2	136	前進搬送・混合エレメント	
3	139	前進搬送・混合エレメント	
4	135	前進搬送・混合エレメント	
5	119	前進搬送・切断エレメント	
6	117	前進搬送・切断エレメント	
7	122	前進搬送・混合エレメント	
8	62	後進混合エレメント	
9	68	後進混合エレメント	
10	71	後進混合エレメント	
11	70	後進混合エレメント	
12	70	後進混合エレメント	
13	69	後進混合エレメント	
14	69	後進混合エレメント	
15	67	後進混合エレメント	
16	67	後進混合エレメント	
17	124	前進搬送・切断エレメント	
18	185	ニュートラル切断エレメント	

*図9のコンパス146で定義される垂直からの角度(°)

上記ミキサーに、デーリング(Doering)ポンプ($p = 240 \text{ psi}$)を用いてシリコーン生ゴムを40ポンド/時(1 lbs/hr)の速度で投入し、減量式アクリソン(Acrisson)フィーダーを用いて前処理ヒュームドシリカを601bs/hrの速度で投入す

る。いずれの供給原料も室温である。ミキサーを300 rpm、アンペア数15.5～16.5で作動させる。排出温度を81～89°Fに上げ、シェル温度を約73°Fに保つ。タップ密度が0.40～0.42の7つの試料を調製する。

【0048】例2

ヒュームドシリカ63部とポリマー生ゴム100部を用いて例1のドレイス混合段階を繰り返す。ドレイス混合段の生成物を直ちにバンパリーミキサーに投入し、メトキシ末端流体処理剤2.5部、シラノール流体処理剤/加工助剤2.5部及びビニルメトキシシラン架橋剤0.8部とコンパウンドィングした後、触媒1.2部を用いて350°Fで10分間硬化させ、450°Fで後硬化

させる。75ジュロメーター試料で得られた物性を表2に示す。

【0049】例3

比較のため、充填材とポリマーを直接バンパリーミキサーに入れ、同じ材料とコンパウンドィングし、例2と同じように硬化させる。75ジュロメーター試料で得られた物性を表2に示す。

表 2

性質/例	2	3
ショア-A硬さ	72	76
伸び	395	366
100%モジュラス	322	355
引張	1277	1302
引裂B	148	153
比重	1.226	1.203

例4

ヒュームドシリカ63部とポリマー生ゴム100部を用いて例1のドレイス混合段階を繰り返す。ドレイス混合段の生成物を直ちにバンパリーミキサーに投入し、メトキシ末端流体処理剤2.5部、シラノール流体処理剤/加工助剤2.5部及びビニルメトキシシラン架橋剤0.8部とコンパウンドィングする。これらの材料からなる

試料は様々なRPMのバンパリーミキサーでコンパウンドィングする。コンパウンドィングした試料を2,4-ジクロロベンゾイルパーオキサイド1.5部で260°Fで12分間硬化させる。得られたシート状試料を20°Cで4時間後硬化させる。75ジュロメーター試料に対する物性を表3に示す。

表 3

性質/例RPM	1400	2000	2800	3200
ショア-A硬さ	76	77	75	75
伸び	324	347	308	323
100%モジュラス	410	407	385	366
引張	1327	1398	1210	1220
引裂B	134	126	126	130
比重	1.207	1.209	1.198	1.199

例5

ヒュームドシリカ63部とポリマー生ゴム100部を用いて例1のドレイス混合段階を繰り返す。ドレイス混合段の生成物を噛合型同方向回転二軸押出機に連続的に投入してコンパウンドィングした後、往復式單軸押出機に連続的に投入して均質化及びストリッピングを行う。最終生成物はビニルジオール架橋剤1.35部、シラノール流体処理剤/加工助剤2.0部及び架橋剤/可塑剤としてのメチルビニル酸3部を含んでいる。生成物は揮発分<1%である。生成物を2,4-ジクロロベンゾイルパーオキサイド1.5部で260°Fで17分間硬化させる。製品シートを200°Cで4時間後硬化させる。75ジュロメーター試料での物性を表4に示す。

【0050】例6

ヒュームドシリカ61部とポリマー生ゴム100部を用いて例1のドレイス混合段階を繰り返す。ドレイス混合段の生成物を噛合型同方向回転二軸押出機に連続的に投入してコンパウンドィングした後、非噛合型異方向回転二軸押出機に連続的に投入して均質化及びストリッピングを行う。最終生成物はシラノール流体処理剤/加工助剤1.0部と架橋剤/可塑剤としてのメチルビニル酸0.5部を含んでいる。生成物は揮発分<1%である。生成物を2,4-ジクロロベンゾイルパーオキサイド1.5部で260°Fで17分間硬化させる。製品シートを200°Cで4時間後硬化させる。40ジュロメーター試料での物性を表4に示す。

表 4

性質/例	5	6
ショア-A硬さ	70.1	37.8
伸び	327	519
100%モジュラス	420	108
引張	1467	1078

引裂B

比重

これらの結果が示す通り、高速混合段でプレミックスを連続的に調製して自由流動性の粒状コンセントレートを形成し、連続的にコンパウンド装置に投入すれば、熱硬化性シリコーン組成物を調製することができる。

【0051】本発明の好ましい実施形態について説明してきたが、本発明は変更及び修正が可能であり、実施例の細部に限定されるものではない。本発明は、特許請求の範囲に属する変更及び改変を包含する。

【図面の簡単な説明】

【図1】 連続熱硬化性シリコーン組成物コンパウンド装置及び装置の概略図である。

【図2】 連続熱硬化性シリコーン組成物コンパウンド装置及び装置の概略図である。

【図3】 連続環状層ミキサーの側面立面図である。

【図4】 ミキサー要素の透視図である。

【図5】 ミキサー要素の透視図である。

【図6】 エレメントの概略説明図であり、エレメントのピッチを示している。

【図7】 図3のA-A線を通して見た概略説明図である。

【図8】 図3のB-B線を通して見た概略説明図である。

【図9】 エレメントのピッチを決定するための基準コンパスである。

【符号の説明】

1 2 高速混合段

1 4 押出機段

1 6, 6 0 減量フィーダー

1 2 3 6 9

1. 2 1 1. 1 0 6

2 0 シリコーンポリマー

2 2, 6 6 処理剤

2 4, 7 0 自由流動性プレミックス

2 6 添加剤

3 0, 8 0 熱硬化性シリコーンポリマー組成物

5 2 連続環状層ミキサー

5 4 第二ミキサー

5 6, 5 8 押出機

6 2 充填材

1 0 2 連続環状層ミキサー

1 0 4 円筒状ハウジング

1 0 6 中央縦方向シャフト

1 1 2 原料供給口

1 1 4 排出口

1 1 6, 1 4 0 混合エレメント

1 1 8, 1 2 8 ステム

1 2 2 末端扇形ヘッド

1 2 4, 1 5 6 切断エレメント

1 3 4 切断エッジ

1 3 8 供給(第一)セクション

1 4 2 軸方向搬送方向

1 5 4 第二セクション

1 5 8 第三セクション

1 6 0 後進ピッチの搬送エレメント

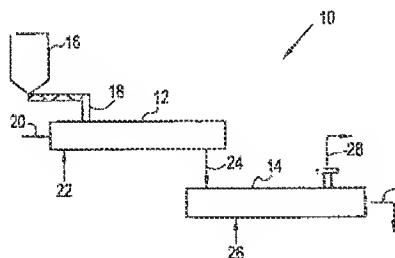
1 6 2 第四セクション

1 6 4 後進ピッチの切断エレメント

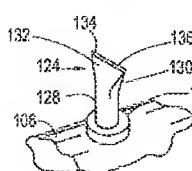
1 6 6 前進ピッチの混合エレメント

1 6 8 ニュートラルエレメント

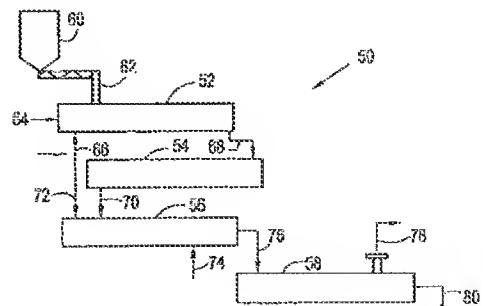
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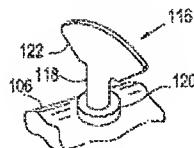
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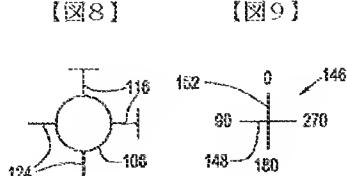
【図7】



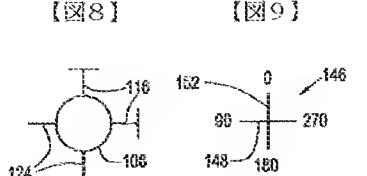
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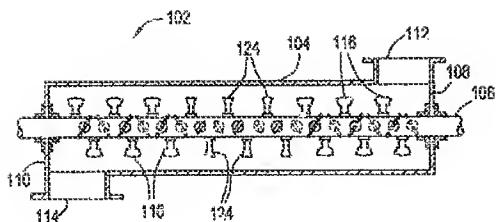
【図8】



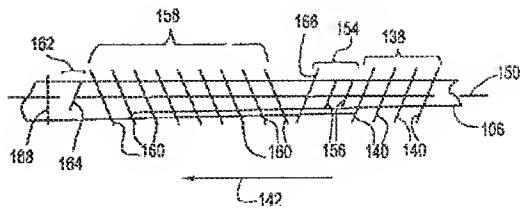
【図9】



【図3】



【図6】



フロントページの続き

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【外國語明細書】

1. Title of Invention

CONTINUOUS PREPARATION OF HEAT-VULCANIZABLE SILICONE COMPOSITIONS

2. Claims

1. A process of compounding a filled heat-vulcanizable silicone composition, comprising:

continuously feeding filler and silicone polymer to a high speed mixing stage to form a free-flowing particulate concentrate; and

continuously discharging said free-flowing particulate concentrate from said mixing stage to a compounding apparatus.

2. The process of claim 1, comprising, continuously compounding said concentrate in said compounding apparatus to form a filled heat-vulcanizable silicone composition.

3. The process of claim 1, wherein said mixing stage comprises a shearing and stirring mechanism.

4. The process of claim 1, wherein said mixing stage comprises a continuous annular layer mixer.

5. The process of claim 1, wherein said compounding apparatus is a helically driven extruder mechanism.

6. The process of claim 1, wherein said mixing stage comprises two continuous annular mixers connected in sequence, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixers for a residence time of between about 5 s and about 10 min to form a premix; and

discharging said premix to said compounding apparatus.

7. The process of claim 1, wherein said mixing stage comprises at least two continuous annular mixers connected in sequence, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixers for a residence time of between about 10 s and about 3 min to form a premix; and

discharging said premix to said compounding apparatus.

8. The process of claim 1, wherein said mixing stage comprises two continuous annular mixers connected in sequence, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixers for a residence time of between about 20 s and about 3 min to form a premix; and

discharging said premix to said compounding apparatus.

9. The process of claim 1, wherein said mixing stage is a continuous annular layer mixer and said compounding apparatus is a helical driven extruder mechanism.

10. The process of claim 9, wherein said continuous annular layer mixer is adjacent and connected to said compounding apparatus.

11. The process of claim 9, wherein said continuous annular layer mixer abuts and connects to said compounding apparatus.

12. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer at an element tip speed of between about 3 m/s and about 100 m/s to form a premix; and

discharging said premix to said compounding apparatus.

13. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer at an element tip speed of between about 10 m/s and about 80 m/s to form a premix; and

discharging said premix to said compounding apparatus.

14. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer at an element tip speed of between about 15 m/s and about 60 m/s to form a premix; and

discharging said premix to said compounding apparatus.

15. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer for a residence time of between about 3 s and about 5 min to form a premix; and

discharging said premix to said compounding apparatus.

16. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer for a residence time of between about 5 s and about 1 min to form a premix; and

discharging said premix to said compounding apparatus.

17. The process of claim 9, comprising:

mixing said filler with said silicone polymer in said continuous annular layer mixer for a residence time of between about 20 s and about 45 s to form a premix; and

discharging said premix to said compounding apparatus.

18. The process of claim 9, wherein said continuous annular layer mixer has a sequence of at least a first section comprising a mixing element, a second section comprising a cutting element and a third section comprising a mixing element.

19. The process of claim 9, wherein said continuous annular layer mixer has a sequence of at least a first section comprising a forward pitched mixing element, a second section comprising a forward pitched cutting element or neutral cutting element and a third section comprising a rearward pitched mixing element.

20. The process of claim 19, wherein said continuous annular layer mixer comprises about 5 to about 80% first section elements, about 10 to about 85% second section elements and about 0 to about 75% third section elements.

21. The process of claim 19, wherein said continuous annular layer mixer comprises about 10 to about 65% first section elements, about 10 to about 65% second section elements and about 10 to about 75% third section elements.

22. The process of claim 19, wherein said continuous annular layer mixer comprises about 15 to about 55% first section elements, about 10 to about 45% second section elements and about 20 to about 65% third section elements.

23. The process of claim 19, wherein said continuous annular layer mixer additionally comprises a final section comprising forward pitched cutting or forward pitched mixing elements.

24. A process of compounding a filled heat-vulcanizable silicone composition, comprising:

mixing a filler with a silicone polymer in a continuous annular layer mixer at an element tip speed of between about 3 m/s and about 100 m/s to form a premix; and

discharging said premix to a next processing apparatus.

25. The process of claim 24, wherein said tip speed is between about 10 m/s and about 80 m/s.

26. The process of claim 24, wherein said tip speed is between about 15 m/s and about 80 m/s.

27. A process of forming a premix for preparing a filled heat-vulcanizable silicone composition, comprising:

mixing a filler with a silicone polymer in a continuous annular layer mixer; and

discharging filled silicone polymer premix from said mixer.

28. The process of claim 27, wherein said premix is discharged to a storage area.

29. The process of claim 27, wherein said premix is discharged and transported to an area for further processing.

30. The process of claim 27, wherein said premix is discharged and transported to an area for further processing.

31. A continuous annular layer mixer, comprising a sequence of at least a first section comprising a mixing element, a second section comprising a cutting element and a third section comprising a mixing element.

32. The continuous annular layer mixer of claim 31, comprising a sequence of at least a first section comprising a forward pitched mixing element, a second section comprising a forward pitched cutting element or neutral cutting element and a third section comprising a rearward pitched mixing element.

33. The continuous annular layer mixer of claim 31, comprising about 5 to about 80% first section elements, about 10 to about 85% second section elements and about 0 to about 75% third section elements.

34. The continuous annular layer mixer of claim 31, comprising about 10 to about 65% first section elements, about 10 to about 65% second section elements and about 10 to about 75% third section elements.

35. The continuous annular layer mixer of claim 31, comprising about 15 to about 55% first section elements, about 10 to about 45% second section elements and about 20 to about 65% third section elements.

36. The continuous annular layer mixer of claim 31, additionally comprising a final section comprising forward pitched cutting or forward pitched mixing elements.

37. A compounding apparatus, comprising:

a first stage continuous annular layer mixer; and

at least one subsequent stage comprising an extruder connected to said first stage to permit continuous discharge of processed material from said first stage to said second stage.

38. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer comprises a sequence of at least a first section comprising a mixing element, a second section comprising a cutting element and a third section comprising a mixing element.

39. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer comprises a sequence of at least a first section comprising a forward pitched mixing element, a second section comprising a forward pitched cutting element or neutral cutting element and a third section comprising a rearward pitched mixing element.

40. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer comprises about 5 to about 80% first section elements, about 10 to about 85% second section elements and about 0 to about 75% third section elements.

41. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer comprises about 10 to about 65% first section elements, about 10 to about 65% second section elements and about 10 to about 75% third section elements.

42. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer comprises about 15 to about 55% first section elements, about 10 to about 45% second section elements and about 20 to about 65% third section elements.

43. The compounding apparatus of claim 37, wherein said first stage continuous annular mixer additionally comprises a final section comprising forward pitched cutting or forward pitched mixing elements.

44. The compounding apparatus of claim 38, wherein said first stage continuous annular mixer wherein said mixing element comprises a stem extending to terminate in a distal fan-shaped head and said cutting element comprises a stem that flares outwardly and bevels inwardly to form a cutting edge at its distal head.

45. The compounding apparatus of claim 37, wherein said second stage comprises a co-rotating, intermeshing double screw extruder.

46. The compounding apparatus of claim 37, wherein second stage comprises a co-rotating, non-intermeshing double screw extruder.

46. The compounding apparatus of claim 37, wherein said stages are separate, adjacent stages.

47. The compounding apparatus of claim 37, wherein said stages are contiguous abutting stages.

48. The compounding apparatus of claim 37, wherein said first stage comprises a plurality of mixers arranged to operate in sequence.

49. The compounding apparatus of claim 37, wherein said first stage comprises a plurality of mixers, wherein at least two mixers are arranged to operate in tandem.

50. The compounding apparatus of claim 37, wherein said at least one subsequent stage comprises a co-rotating intermeshing double screw extruder, a counter-rotating double screw extruder or a single screw extruder.

51. The compounding apparatus of claim 37, wherein said at least one subsequent stage comprises a co-rotating intermeshing double screw extruder or a single reciprocating screw extruder.

3. Detailed Description of Invention

BACKGROUND OF THE INVENTION

The invention relates to a process for continuously preparing heat-vulcanizable silicone compositions.

A heat-vulcanizable silicone composition comprises a high viscosity silicone polymer, an inorganic reinforcing filler and various additives that aid processing or impart desired final properties to the composition. A vulcanizing agent can be added and the composition heat-cured to fabricate silicone rubber moldings such as gaskets, medical tubing and computer keypads.

Typically, the heat-vulcanizable silicone composition is produced by kneading a high-viscosity polydiorganosiloxane, the inorganic filler and additives by means of a batch kneading machine such as a high intensity Banbury mixer or a low intensity double arm dough mixer. In this process, polydiorganosiloxane, inorganic filler, treating agents and additives are batch mixed until desired properties are obtained. In Kasahara *et al.*, U.S. Pat. 5,198,171, a preconcentrate of polydiorganosiloxane, inorganic filler and treating agents is formed by a high speed mechanical shearing mixer. The resulting premix is further compounded in a same-direction double screw extruder. The premix is formed in a first step wherein a diorganopolysiloxane having a viscosity at 25°C of 1×10^6 cP or more, an inorganic filler and a treating agent are mixed in a high speed mechanical shearing machine to provide a flowable particulate mixture in which each ingredient is present in a substantially uniform, finely dispersed state. The flowable particulate mixture is then fed at a constant feed rate into a kneading and extruding machine that has two screws rotating in the same direction.

A batch process requires long mixing times and large amounts of energy. Non-homogeneous shear and extensional stress across a commercial sized

batch can result in non-uniform size distribution of filler that results in variations in properties. Batches processed at different times may be characterized by different physical properties. The batch process is labor, energy and capital intensive and produces materials of only marginal consistency.

In Hamada *et al.*, U.S. Pat. 5,409,978, a preconcentrate of polydiorganosiloxane, inorganic filler and treating agents is formed at a temperature in the range of about 200°C to 300°C in a co-rotating continuous double screw extruder. The preconcentrate is then compounded and heat treated at 150°C to 300°C in a counter-rotating, double screw extruder. However, a process that requires two extruders is expensive and requires significant processing area.

However with these processes, throughput is limited. There is a need for a process that provides improved throughput and which can be adapted as a low cost process that can efficiently utilize a single extruder to continuously and consistently produce a full range of both low viscosity and high viscosity silicone elastomers from filler, additive and polymer.

SUMMARY OF THE INVENTION

The invention provides a process that compounds high levels of filler, processing fluid and silicone polymer into homogeneous filled heat-vulcanizable silicone compositions with requisite reinforcing properties and levels of volatiles. The process comprises continuously feeding filler and silicone polymer to a high speed mixing stage to form a free-flowing particulate concentrate. The concentrate is continuously discharged from the mixing stage to a compounding apparatus for further processing.

In another aspect, the invention relates to a process of forming a premix of filler and silicone polymer. In the process, a filler is mixed with a silicone polymer in a continuous annular layer mixer and a filled silicone polymer premix is discharged from the mixer.

In another aspect, the invention relates to a process of compounding a filled heat-vulcanizable silicone composition wherein a filler is mixed with a silicone polymer in a high speed continuous mixer at an element tip speed of between about 3 m/s and about 100 m/s to form a premix. The premix is then discharged to a next processing apparatus.

In another aspect, the invention relates to a continuous annular layer mixer having a sequence of sections comprising at least a first section comprising a forward pitched mixing element, a second section comprising a neutral or forward pitched cutting element and a third section comprising a rearward pitched mixing element.

In yet still another aspect, the invention relates to a compounding apparatus, comprising a first stage continuous annular layer mixer and at least one subsequent stage comprising an extruder connected to the first stage to permit continuous discharge of processed material from the first stage to the second stage.

DETAILED DESCRIPTION OF THE INVENTION

Banbury or dough mixers are known for the batch compounding of fillers with silicone polymers. The compounding operation has two distinct steps; the first step involves the wetting of the filler by the polymer, while the second step involves breaking down of agglomerates and uniform dispersing of filler in polymer. Sufficient dispersion of filler in polymer is important. Any large undispersed agglomerates result in poor mechanical properties since they can act as failure initiating flaws.

In batch or continuous processes, a treating agent can be dispersed along with the silicone polymer either with or before the addition of filler. In these processes, large interfacial forces develop between silicone polymer and free, unreacted silanol groups present in filler. The treating agent must diffuse through the bulk of the high molecular weight silicone polymer and penetrate a rigid silicone polymer/filler interface to reach the filler for treatment. Mixing intensity must be increased to overcome the large interfacial forces and to permit penetration of the treating agent to access the silanol groups. An increase in mixing intensity causes an undesirable increase in material temperature.

According to the invention, a free-flowing particulate concentrate of silicone and filler is continuously formed in a high feed mixing stage. The concentrate is continuously discharged from the mixing stage to a compounding apparatus for further processing. The mixing stage can comprise a continuous annular layer mixer. A continuous annular layer mixer comprises a cylindrical mixing trough wherein material to be mixed is propelled along a helical path along the axis of the trough in the form of a ring contiguous with the cylindrical mixer wall. A typical continuous annular layer

mixer is disclosed in Erich *et al.*, U.S. Pat. 5,018,673 describing a mixer comprising an essentially horizontally arranged cylindrical housing, which is provided at a first end with a material supply pipe for a continuous supply of material and, at a second end, with a material discharge pipe for a continuous removal of material. The cylindrical housing encloses a mixing apparatus, which is arranged coaxially in the housing. The mixing apparatus is driveable at high speeds. The apparatus comprises mixing tools, which project essentially radially from the apparatus into the vicinity of the housing inner wall. The mixer includes a draw-in zone that is associated with a material supply pipe and a wetting zone that is provided downstream in an axial conveying direction of the draw-in zone. The mixer also includes means provided in the wetting zone for the admission of liquid into a form of a ring of material. The ring is helically conveyed and moved through the mixer on the housing inner wall. The mixer further includes means for the separation of clusters. The means includes a plurality of cutting devices provided in a radial plane relative to the shaft of the mixing apparatus and arranged at equal annular spacings relative to one another around the full circumference of the housing.

In an embodiment of the invention, a continuous annular layer mixer is utilized as a premixing stage to create a fine dispersion of an uncured silicone polymer in a volume of filler. This material can then undergo a phase transformation under compressive, elongational and shear flow fields in an extruder to a compounded state, where dry filler is in a minority phase. First stage densification of the filler results in shorter incorporation times in the extruder and consequently significant improvement in productivity.

The inorganic filler that can be used in the invention can be any inorganic filler used in blends with silicone polymers. Examples of inorganic fillers include a reinforcing silica such as fumed silica or precipitated silica or a silica that has been surface-treated with an organosilicon compound such as an organopolysiloxane, organoalkoxysilane, organochlorosilane or a hexaorganodisilazane. The filler can be diatomaceous earth, finely crushed

quartz, aluminum oxide, titanium oxide, iron oxide, cerium oxide, cerium hydroxide, magnesium oxide, zinc oxide, calcium carbonate, zirconium silicate, carbon black or ultramarine. A single filler or a combination of fillers can be used to reinforce the silicone polymer.

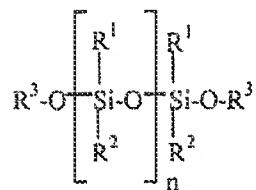
The amount of the filler can be in the range of from about 5 to about 200 parts by weight, desirably from about 10 to about 100 parts by weight and preferably from about 20 to about 60 parts by weight, per 100 parts by weight of silicone polymer.

Residual silanol groups on the surface of a filler can govern strength of hydrogen bonds between the silica and hydroxyl or oxygen groups in the silicone polymer chain. High concentrations of residual silanols in a filler cause "structuring" or "crepe hardening" of the final product in storage. This effect leads to difficulties in the processing of the material after it has been stored for extended periods. If the concentration of silanol functional groups in a filler is too high, a treating agent can be added to reduce the groups to a required concentration. The silanol reactant treating agent can react to reduce available groups to a concentration of between about 8 to about 2 hydroxyl groups/(nanometer)² of filler, preferably between about 7 to about 3 hydroxyl groups/(nanometer)² of filler. The surface-treated silica is a preferred filler in the invention, in an amount from about 10 to about 100 parts by weight, preferably from about 20 to about 60 parts by weight, per 100 parts by weight of silicone polymer.

The treating agent can be mixed into the filler to reduce filler silanol groups, to improve dispensability of the filler and/or to reduce the time required for aging of the silicone rubber, to prevent crepe hardening and/or to regulate plasticity. The treating agent can be an organosilane, a low-viscosity polysiloxane or a silicone resin, which has a silanol group and/or an alkoxy group having 1 to 6 carbon atoms. Examples include diphenyl-silanediol, dimethylsilanediol, methyltriethoxysilane and phenyltrimethoxysilane. The low-viscosity polysiloxane may contain one or more kinds of organic groups

selected from a methyl group, a phenyl group, a vinyl group and a 3,3,3-trifluoropropyl group. The viscosity of the polysiloxane measured at 25°C is in the range of from about 1 to about 300 cP, preferably from about 5 to about 100 cP. The treating agent can be added in an amount of from 0.1 to 100 parts by weight, desirably from 0.5 to about 50 parts by weight and preferably from about 1.0 to about 20 parts by weight per 100 parts by weight of the filler. Preferred silanol-reactant treating agents include silanol-stopped polydimethylsiloxane, octamethylcyclotetrasiloxane (D₄) and hexamethyldisilazane (HMDS).

The silicone polymer used in the compositions of the present invention can be represented by recurring units of Formula I:



Formula I

wherein, R¹ independently at each occurrence represents C₁₋₄ alkyl, or C₂₋₄ alkylene; R² independently at each occurrence represents C₁₋₄ alkyl, C_{1-C₄} haloalkyl or C₂₋₄ alkylene; R³ independently at each occurrence represents H, C₁₋₁₀ alkyl, C₂₋₄ alkylene, C₄₋₆ cycloalkyl, OH or C_{1-C₄} haloalkyl; and n represents an integer from 1,000 to 20,000.

A further preferred composition comprises a silicone polymer wherein, R¹ independently at each occurrence represents, CH₃ or CH=CH₂; R² independently at each occurrence represents, CH₃, CH=CH₂ or CH₂CH₂CF₃; R³ independently at each occurrence represents CH₃, CH=CH₂, OH or CH₂CH₂CF₃; and n represents an integer from about 4,000 to about 10,000.

Another embodiment provides a composition wherein the vinyl content of the silicone polymer ranges from about 0.05% to about 0.5 % by weight of the silicone polymer.

The heat-vulcanizable silicone composition can also include other additives such as heat-resistance improvers such as oxides, hydroxides and fatty acid salts of metals, vulcanization reverse inhibitors, flame retardants such as platinum compounds, discoloration preventive agents, plasticizers such as silicone oil, internal release agent such as metal soaps, pigments and dyes.

Features of the invention will become apparent from the following drawings and detailed discussion, which by way of example without limitation describe embodiments of the present invention.

FIG.1 schematically represents a process according to the present invention

In FIG. 1, the apparatus 10 of the invention includes a high speed mixing stage 12 and an extruder stage 14. High speed mixing stage 12 can represent a continuous annular layer mixer and can represent a single mixer or a plurality of mixers arranged to operate in sequence. The extruder stage 14 can be one or more of a co-rotating intermeshing double screw extruder, a counter-rotating double screw extruder or a single screw extruder. Preferably, the extruder stage 14 is a co-rotating intermeshing double screw extruder or a single reciprocating screw extruder. When the extruder stage includes a plurality of extruders, they can be connected sequentially or in tandem.

In the process of the invention, filler is contained in loss-in-weight feeder 16 and is fed 18 along with silicone polymer 20 and treating agent 22, into mixing stage 12.

In the mixing stage 12, the polymer, filler and agent are subjected to a high speed, high intensity force to produce a free flowing powder premix 24.

Adequate tip speed and residence time are required to break down the material and to coat the filler with polymer and wet the materials with treating agent. The materials can be mixed at an element tip speed of between about 3 m/s and about 100 m/s to form the premix. Desirably, the element tip speed is between about 10 m/s and about 80 m/s and preferably between about 15 m/s and about 60 m/s. Residence is the time required for material to pass through the mixer. Residence time can be between about 3 seconds (s) to about 5 minutes (min) when a single mixer is used. The residence time for a single mixer can be from about 5 s to about 1 min and preferably can be between about 20 s to about 45 s. The mixing stage 12 can comprise a plurality of mixers. When two mixers are used in sequence, residence time for the two can be from about 5 s to about 10 min or the residence time can be from about 10 s to about 5 min or preferably 20 s to about 3 min. The mixing stage 12 can produce a product with a tap density of about 0.3 to about 0.6 or about 0.35 to about 0.55 or even 0.36 to about 0.48.

Advantageously, the premix 24 can be used in a continuous process (as illustrated herein) or can be stored and distributed for later use. In FIG. 1, the premix 24 is fed to extruder stage 14 where it is compounded with additives 26 and devolatilized to produce a heat vulcanizable silicone polymer composition 30.

FIG. 2 illustrates another embodiment of the invention. The apparatus 50 of FIG. 2 includes continuous annular layer high speed mixer 52 and a second mixer 54 arranged in sequence. Two or more mixers can be utilized to provide increased residence time to provide a more consistent premix. The FIG. 2 apparatus includes extruder 56 connected in sequence down stream of mixers 52, 54 and subsequent extruder 58.

In the process illustrated in FIG. 2, loss-in-weight feeder 60 meters filler 62 into first mixer 52 to be mixed with polymer 64 and treating agent 66. The product from mixer 52 is charged 68 into mixer 54 where a free flowing powder premix 70 is produced, which is charged to extruder 56 where

additional treating agent is added 72 for further filler treatment. Additional polymer can be added (not shown) in this step to make low durometer material. Processing aids and other additives are added 74 in this step to produce a product 76 which is charged into extruder 58 for devolitilization 78. Extruder 58 produces a heat vulcanization silicone polymer composition 80 for further use.

FIGS. 3 to 8 show a continuous annular layer mixer and associated elements.

FIGs. 4 and 5 are representations of processing elements that can be included in a mixer that can be used in the invention. FIG. 3 is a side elevational view of a continuous annular layer mixer 102 showing a placement of the elements of FIGs. 4 and 5.

In FIG. 3, mixer 102 comprises a cylindrical housing 104 with central longitudinal shaft 106. The housing 104 is sealed at transverse ends by end walls 108, 110. The shaft 106 projects through both ends of the housing 104 and is sealed by end walls 108, 110. Material feed 112 is attached to an upper part of housing 104 to open substantially tangentially into the interior of the housing 104 and discharge 114 is provided at a lower end of the housing 104 substantially tangentially to the interior of the housing 104 and opening out from the interior of the housing 104.

Processing elements of various designs are provided on shaft 106 of mixer 102. FIG. 4 shows a mixing element 116 that extends from rotatable shaft 106 and projects radially from shaft 106 within the continuous annular layer mixer 102 of FIG. 3. Mixing elements 116 are axially aligned at 90° intervals as viewed along the shaft 106 longitudinal axis and as shown in FIGs. 7 and 8. Mixing element 116 includes stem 118 extending from base 120 to terminate in distal fan-shaped head 122. The mixing element 116 is shown extending perpendicular to the base 120 with an angled paddle head 122. The element 116 is fixed in the base 120 at a head pitch angle to provide a relatively

increased conveying (propulsive) function or backmixing function, as the case may be. Various pitches of elements and descriptions of function are provided hereinafter with reference to FIGs. 6 to 9.

FIG. 5 shows cutting element 124 extending from base 126 and directed radially from the shaft 106 within the mixer 102. The cutting element 124 includes stem 128 that flares outwardly 130 and bevels inwardly 132 to form a cutting edge 134 at its distal head 136. The element 124 is shown extending perpendicular. The element 124 can be fixed at a cutting edge pitch angle so as to control conveying and backmixing functions, as described with reference to FIG. 6 and FIG. 9. The elements 124 are axially aligned at 90° intervals as viewed along the shaft 106 longitudinal axis and as shown in FIG. 8.

FIG. 6 is a schematic representation of elements illustrating element pitch with respect to the mixer shaft 106. FIG. 6 shows a first draw-in section (first section) 138 of mixer 106, wherein mixing elements 140 are provided that are set with heads in an axial conveying direction 142. Filler/treating agent/silicone polymer material is charged into the mixer 106 via the feed 112 shown in FIG. 3 at first section 138 and is accelerated and set in motion in an axial conveying direction 142 by the mixing elements 140. The FIG. 6 illustrates pitch of element heads 122 and 136 from an axis defined by the longitudinal axis 152 of the mixer shaft 106 where degree of pitch is defined by FIG. 9. Elements pitched at an angle between 90° and less than 180° impart a conveying function, while elements pitched at an angle between 0° and less than 90° impart a holding function. The mixing elements 140 extend close to the inner wall of housing 104 to avoid dead space and, as shown in FIG. 7, the mixing elements 140 are spaced around the circumference of shaft 106 at about 90° intervals.

The mixing elements 140 are set into a conveying direction at an angle of about 138° from a perpendicular defined by the compass 146 of FIG. 9, wherein abscissa 148 coincides with mixer shaft longitudinal axis 150 and ordinate 152 is perpendicular to the axis 150. Rotation of conveying element

140 creates a centrifugal force which flings material into the form of a ring at a radial outer end of element 140. Element 140 pitch then causes the charged material in the form of the ring to advance helically through the mixer 102 interior.

A second section 154 of the mixer 102 includes cutting elements 156 that are pitched at a conveying direction angle of about 118° from perpendicular. The cutting elements 156 are circumferentially spaced at about 90° around shaft 106 as shown along with conveying elements 140 in FIG. 9 and extend close to inner wall of the housing 104 to avoid dead space. The elements 156 act to separate clusters of material to accelerate wetting of filler.

A third section 158 comprises rearward pitched conveying elements 160 to provide backmixing and increased residence time.

In an embodiment of the invention, the continuous annular layer mixer 102 has a sequence of at least a first section comprising mixing elements, a second section comprising cutting elements and a third section comprising mixing elements. The sections can include other elements besides the specified mixing or cutting elements. For example, the second section can comprise cutting and mixing elements. The first section can comprise forward pitched elements, the second section can comprise forward and neutral elements and the third section can comprise rearward pitched elements for increased residence time. The total elements of the continuous annular layer mixer 102 can comprise about 5 to about 80% first section elements, about 10 to about 85% second section elements and about 0 to about 75% third section elements; desirably about 10 to about 65% first section elements, about 10 to about 65% second section elements and about 10 to about 75% third section elements; or preferably about 15 to about 55% first section elements, about 10 to about 45% second section elements and about 20 to about 65% third section elements.

FIG. 6 illustrates an embodiment of the invention, wherin the continuous annular layer mixer 102 has a sequence of a first section 138 comprising forward pitched mixing elements 140, a second section 154 comprising forward pitched cutting elements 156 and a third section 158 comprising rearward pitched mixing elements 160. As shown in FIG. 6, the mixer 102 can terminate in a fourth section 162 comprising a forward pitched cutting element 164 followed by a neutral element 168 for ejecting the premix. The second section 154 can also include a forward pitched mixing element 166.

According to the invention, premixing in the continuous annular layer mixer creates a fine dispersion of an uncured polymer in a volume of filler. This material then undergoes a phase transformation under compressive, elongational and shear flow fields in an extruder to a compounded state where the dry filler is a minority phase. Densification of the filler in the annular layer mixer results in shorter incorporation times and consequently significant improvement in productivity.

These and other features will become apparent from the following detailed discussion, which by way of example without limitation describes preferred embodiments of the present invention. In the Examples, premix quality is characterized by tap density, BET surface area, solution and dry powder particle size. The premix material is examined by scanning electron microscopy, transmission electron microscopy and compression testing.

Example 1

A Drais KTT continuous annular layer mixer is provided with the element configuration described in Table 1.

Table 1

Element No./Description	Angle*	Description
1	139	forward conveying and mixing element
2	136	forward conveying and mixing element
3	139	forward conveying and mixing element
4	136	forward conveying and mixing element
5	119	forward conveying and cutting element
6	117	forward conveying and cutting element
7	122	forward conveying and mixing element
8	62	rearward mixing element
9	68	rearward mixing element
10	71	rearward mixing element
11	70	rearward mixing element
12	70	rearward mixing element
13	69	rearward mixing element
14	69	rearward mixing element
15	67	rearward mixing element
16	87	rearward mixing element
17	124	forward conveying and cutting element
18	186	neutral cutting element

* angle in degrees from perpendicular as defined by the compass 146 of FIG. 9

A silicone gum is charged into the mixer by means of a Doering pump ($p = 240$ psi) at a rate of 40 lbs/hr and pretreated fumed silica is charged by means of a loss in weight Acrisson feeder at a rate of 60 lbs/hr. Both feeds are at room temperature. The mixer is operated at 3000 rpm at an amperage of 15.5 to 16.5. Discharge temperature increases from 81°F to 89°F and shell temperature is consistent at about 73°F . Seven samples are prepared with a tap density of between 0.40 to 0.42.

Example 2

The Drais mixing step of Example 1 is repeated with 63 parts of fumed silica and 100 parts of a polymer gum. The product from the Drais mixing

step is immediately charged into a Banbury mixer where it is compounded with 2.5 parts methoxy stopped fluid treating agent, 2.5 parts of silanol fluid treating agent/processing aid and 0.8 parts of vinyl methoxy silane crosslinker and then cured with 1.2 parts catalyst for 10 minutes at 350°F and post baked at 450°F. Physical properties obtained for a 75 Durometer product are provided in Table 2.

Example 3

As a comparison, filler and polymer are added directly to the Banbury mixer and are compounded with the same materials and cured in the same manner as in Example 2. Physical properties obtained for a 75 Durometer product are provided in Table 2.

Table 2

Property/Example	2	3
Shore A Hardness	72	76
Elongation	395	366
100% Modulus	322	355
Tensile	1277	1302
Tear B	148	153
Specific Gravity	1.226	1.203

Example 4

The Drais mixing step of Example 1 is repeated with 63 parts of fumed silica and 100 parts of a polymer gum. The product from the Drais mixing step is immediately charged into a Banbury mixer where it is compounded with 2.5 parts methoxy stopped fluid treating agent, 2.5 parts of silanol fluid treating agent/processing aid and 0.8 parts of vinyl methoxy silane crosslinker. Samples of the materials are compounded in the Banbury mixer

at various RPM's. The compounded samples are cured with 1.5 parts of 2,4-dichlorobenzoyl peroxide for 12 minutes at 260°F. The resulting sheet samples are post baked at 200°C for 4 hours. Physical properties for 75 Durometer samples are provided in Table 3.

Table 3

Property/Example RPM's	1400	2000	2800	3200
Shore A Hardness	78	77	75	75
Elongation	324	347	308	323
100% Modulus	410	407	385	366
Tensile	1327	1398	1210	1220
Tear B	134	128	126	130
Specific Gravity	1.207	1.209	1.198	1.199

Example 5

The Drais mixing step of Example 1 is repeated with 63 parts of fumed silica and 100 parts of a polymer gum. The product from the Drais mixing step is continuously charged into a twin screw, co-rotating intermeshing extruder for compounding and then continuously into a single screw reciprocating extruder for homogenization and stripping. The final product includes 1.35 parts vinyl diol crosslinker, 2.0 parts of silanol fluid treating agent/processing aid and 3 parts of a methylvinyl source as a crosslinker/plasticizer. The product has <1% volatiles. The product is cured with 1.5 parts of 2,4-dichlorobenzoyl peroxide for 17 minutes at 260°F. Product sheets are post baked at 200°C for 4 hours. Physical properties for 75 Durometer samples are provided in Table 4.

Example 6

The Drais mixing step of Example 1 is repeated with 61 parts of fumed silica and 100 parts of a polymer gum. The product from the Drais mixing step is continuously charged into a twin screw, co-rotating intermeshing

extruder for compounding and then continuously into a counter-rotating, non-intermeshing twin screw extruder for homogenization and stripping. The final product includes 1.0 parts of silanol fluid treating agent/processing aid and 0.5 parts of a methylvinyl source as a crosslinker/plasticizer. The product has <1% volatiles. The product is cured with 1.5 parts of 2,4-dichlorobenzoyl peroxide for 17 minutes at 260°F. Product sheets are post baked at 200°C for 4 hours. Physical properties for 40 Durometer samples are provided in Table 4.

Table 4

Property/Example	5	6
Shore A Hardness	70.1	37.8
Elongation	327	519
100% Modulus	420	108
Tensile	1467	1078
Tear B	123	69
Specific Gravity	1.21	1.106

The results show that a premix can be continuously prepared in a high speed mixing stage to form a free-flowing particulate concentrate that can be continuously charged to compounding apparatus to prepare heat-vulcanizable silicone compositions.

While preferred embodiments of the invention have been described, the present invention is capable of variation and modification and therefore should not be limited to the precise details of the Examples. The invention includes changes and alterations that fall within the purview of the claims.

4. Brief Description of Drawings

FIG. 1 is a schematic representation of a continuous heat-vulcanizable silicone composition compounding process and apparatus;

FIG. 2 is a schematic representation of a continuous heat-vulcanizable silicone composition compounding process and apparatus;

FIG. 3 is a side elevation view of a continuous annular layer mixer;

Figs. 4 and 5 are perspective views of mixer elements;

FIG. 6 is a schematic representation of elements illustrating element pitch;

FIG. 7 is a schematic representation of a view through line A-A of FIG. 3;

FIG. 8 is a schematic representation of a view through line B-B of FIG. 3; and

FIG. 9 is a reference compass for determining element pitch.

FIG. 1

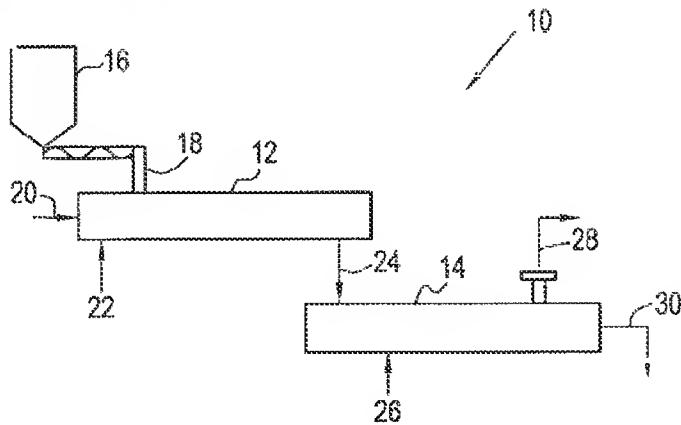


FIG. 2

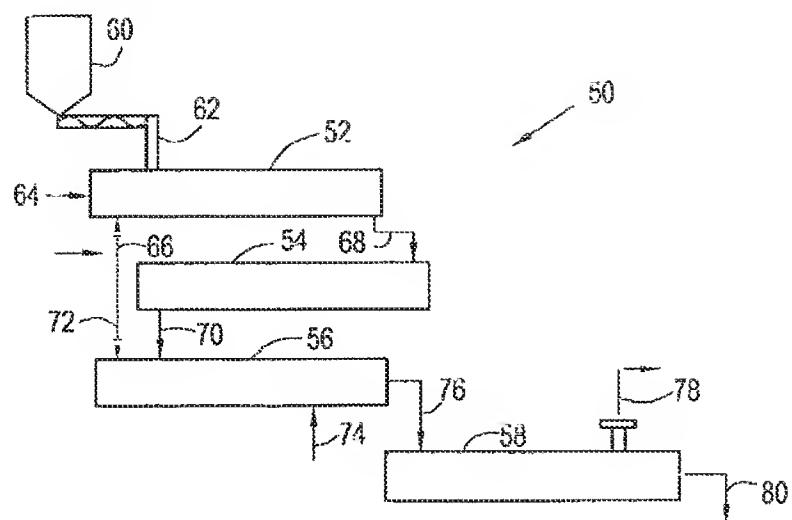


FIG. 3

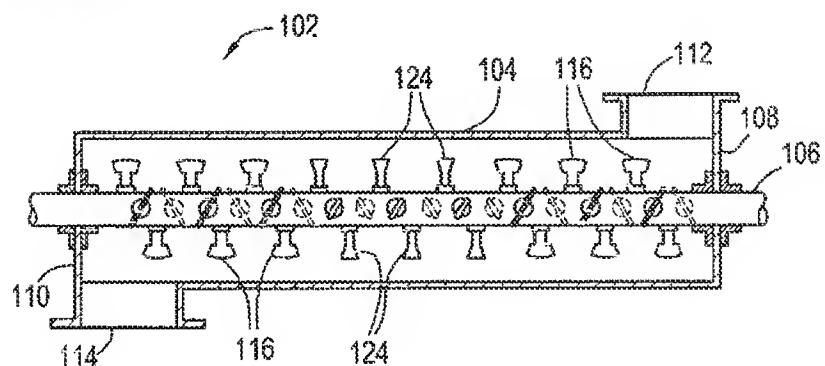


FIG. 4

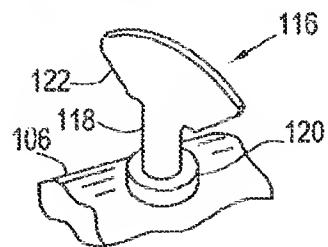


FIG. 5

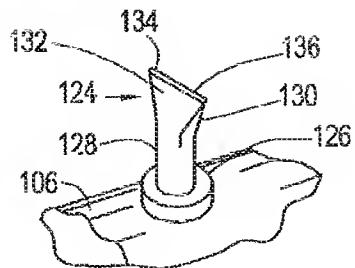


FIG. 6

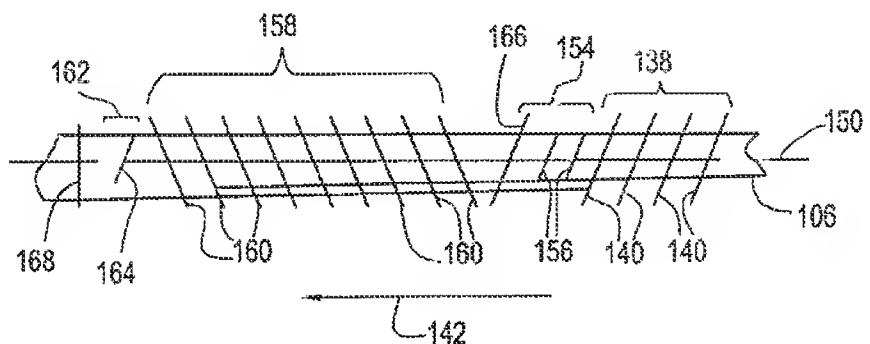


FIG. 7

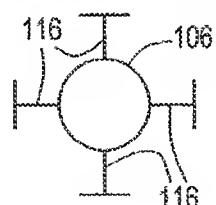


FIG. 8

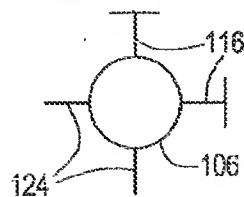
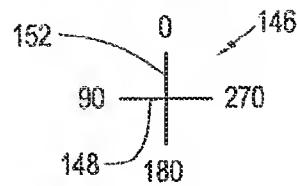


FIG. 9



1. Abstract

High levels of treated fumed silica, processing fluid and high molecular weight silicone polymer are continuously compounded into a homogeneous silica filled heat-vulcanizable silicone composition by forming a premix in a continuous annular layer mixer and continuously discharging the premix into a compounding apparatus for compounding to form the filled heat-vulcanizable silicone composition.

2. Representative Drawing: Figure 1